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Various aspects of the usefulness of the arithmetic and the Kovats retention index systems have been compared in detail. The inclusion of logarithmic function in the definition of the latter system can be more justified from thermodynamic and other theoretical considerations than its elimination in the former. The computation of arithmetic index is a shade faster; it can avoid the use of gas hold-up correction, but cannot be done with any two normal paraffins unlike in the case with retention index. In the determination of the index value from physical properties, like vapour pressure and boiling point of solutes, as well as from correlational graphs of the data for two liquid phases or for two column temperatures, and in the linearity of index with column temperature etc., in short, in many of the multifarious uses, arithmetic index has been found to be as good a parameter as the Kovats retention index.

For the retrieval of arithmetic index from the retention index data available in literature, four methods have been proposed, the simplest possible one requiring the only parameter of slope of the linear plot of logarithm of adjusted retention data against carbon number of the normal paraffins. The value of this slope is affected mildly by the nature of stationary liquids but very strongly by column temperature, which exerts inverse variation over its full working range. The maxima in the difference of the two indices, i.e. (I-I_A) max., which is totally dependent on the slope value has been predicted to be less than 18 at the column temperature of 0°C for all stationary liquids.

Comparison of Retention and Arithmetic Indices—Their Correlations and Relative Usefulness In Gas Chromatography

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Usefulness of Kovats retention index as the most reproducible system for presentation of retention data in gas chromatography is well established[1–9]. Current researches in many laboratories[10–16], including those of present authors[17–19], on the extension of the concept of retention index will no doubt strengthen its peak identification power and widen its scope of applicability.

At the 1969 Informal Symposium of The Gas Chromatography Discussion Group, Harbourn[20] suggested elimination of the logarithmic function in the Kovats formula of retention index (I) and claimed that the resultant expression, termed as the arithmetic index (I_A), is as accurate as I with the added advantage of simplicity and speed of computation. Incidentally, a similarity can be noted in the expression of Harbourn's index and that of Van den Dool and Kratz[21] for the conversion of isothermal retention indices to corresponding programmed temperature values. It is, therefore, necessary to compare the merits and demerits of retention and arithmetic index systems and also to explore their potentialities in the identification of gas chromatographic peaks. To this end, the present investigation was undertaken.

Comparison of Retention and Arithmetic Indices

1. Simplicity and Speed of Calculation

After the introduction of Hupe's monograph[22], computation of retention index does no longer require the use of slide-rule or a logarithm table, but has simply been resolved into drawing three lines in a semi-log paper. Moreover, I can be calculated from the retention data of any two normal paraffins, whereas I_A requires apparently* that pair of adjacent n-paraffins between which the solute elutes. Harbourn claims that air-peak correction of the retention data is not required for the computation of I_A, unlike the case with I. However, gas hold-up of a gas liquid chromatography (GLC)

* See Letter to the Editor on page 65 of this issue and also the "Addendum"

column can be easily calculated from methane peak or from the formula of Hilmi[23].

2. Thermodynamic Content

Kovats[1,2] included logarithmic function in the definition of retention index, mainly because of the established fact of strict linearity of logarithm of adjusted retention data for normal paraffins against its carbon number. Moreover, Kovats index can be derived from basic thermodynamic equations of retention properties[24] and can also be correlated with other elution parameters[25]. On the contrary, arithmetic index appears to represent an abstract formula and is obviously devoid of the thermodynamic content of the elution processes in gas chromatography.

3. Potential for Explaining Inter-molecular Forces Operative in GLC

Conceptually, arithmetic index represents no extension over retention index. Neither of the two indices deals directly with various forces of interaction of solute-solvent molecules which control the separation processes in GLC. Any mechanism to classify column performance in GLC should obviously be based on mathematics of intermolecular forces. The Rohrschneider scale[26] cannot be considered adequate and satisfactory in this regard. If the combination of retention index and Rohrschneider hypothesis has failed to convince the gas chromatographers of its efficacy, it is difficult to see how the incorporation of arithmetic index—as was recently proposed by Bourne[27]—will salvage the Rohrschneider scale in characterizing GLC columns and in predicting the courses of separation. The contribution to index value of a compound may be said to originate ultimately from its constituent atoms, their groupings, nature of bonding, position and steric factors, conformational structures, etc. Any method of prediction of retention or arithmetic index, to be accurate and useful, must have to consider these factors. Schomburg's[28] additivity rule of index increments may be regarded as only a beginning in this direction.

4. Arithmetic Index and Known Uses of Retention Index

It is worthwhile to assess how well and how far arithmetic index can replace retention index in its various applications in gas chromatography.

4.1. As regards accuracy of data, both the index systems are at par. Provided the column variables are controlled rigidly and support effects are absent, both indices should give reproducible and reliable data for identification of gas chromatographic peaks.

4.2. The present authors[18] have shown that the retention indices of hydrocarbons in any stationary liquid bear a fairly good linear relationship with vapour pressure or reduced boiling point, the degree of data scattering diminishing with increased efficiency of classification into well-knit homologues and isomers. It is also highly probable that other types of organic compounds will behave similarly. It can be demonstrated from the data in our hand, that in these graphical correlations I_A is as good as I, and I_A can be determined with a fair degree of accuracy from plots similar to those in Figs. 1 and 2. It can be seen from Fig. 1 that plots of retention and arithmetic indices give very nearly parallel lines. The compounds chosen in the plot of Fig. 1 need not necessarily differ by about 100 index units, as can be

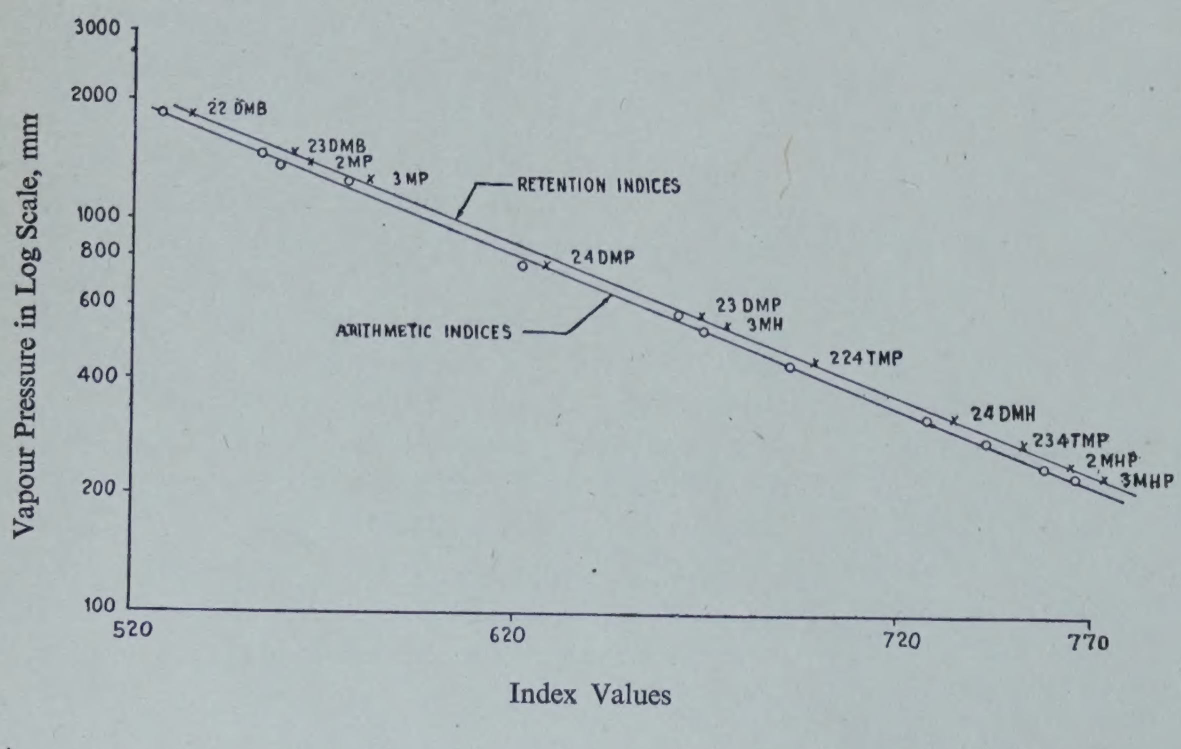


Fig. 1—Relation of Vapour Pressure with Arithmetic and Retention Indices of Solutes in Squalane at 86°C

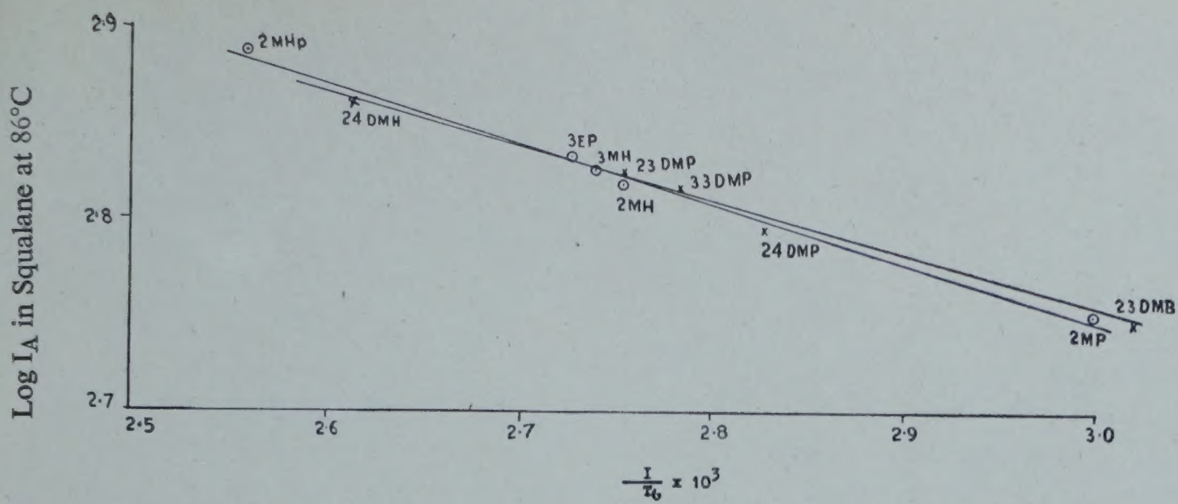


Fig. 2—Relation of I_A with Boiling Points (T_b) of Mono- and Dialkyl Paraffins

seen from Table 1. It can be pointed out that many more hydrocarbons will fit into Fig. 1 or similar plots. Of course, these family plots are only approximate ones, hence the error incurred in linearization of index values is not too large.

4.3. The present authors[17,19] have proposed application of the linearity of retention index with column temperature as a sure parameter for identification of gas chromatographic peaks (this is believed to be equally true with other forms of chromatography). Arithmetic index has been demonstrated to be equally good (in Figs. 3A and 3B) in replacing retention index in the

TABLE 1—Index Values of Hydrocarbons in Squalane at 86°C and Used in Fig. 1

Compounds Abbreviation	Retention Index (I)	Arithmetic Index (I_A)
22 DMB	540	531
23 DMB	571	562
2 MP	571	561
3 MP	586	581
24 DMP	631	623
23 DMP	675	667
3 MH	678	670
224 TMP	694	692
24 DMH	734	725
234 TMP	757	747
2 MHp	765	756
3 MHp	774	765

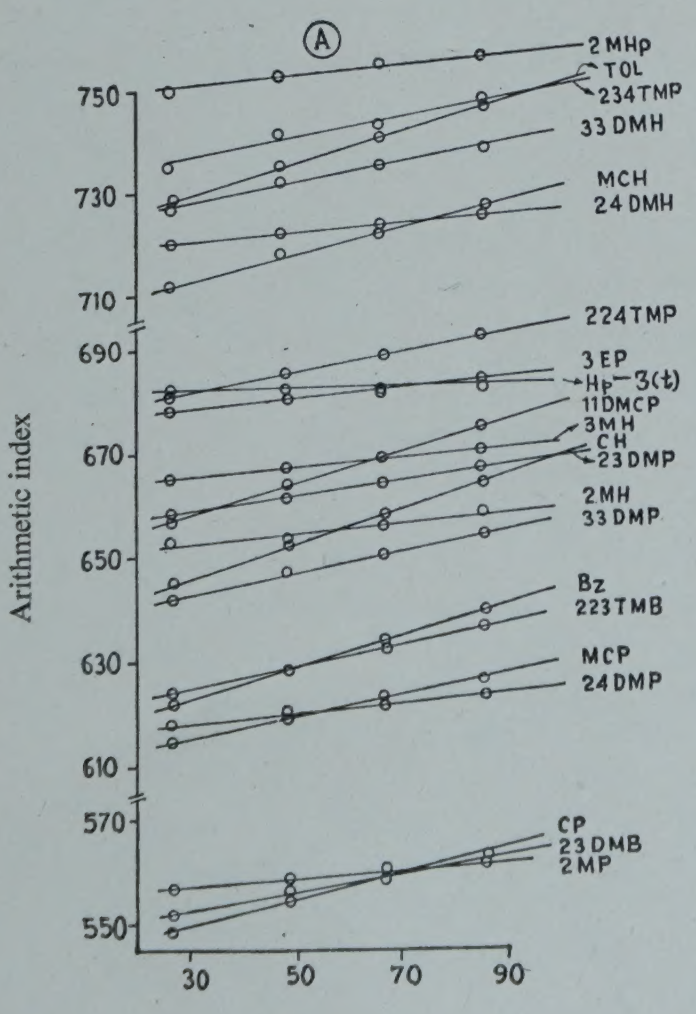


Fig. 3A—Linearity of Arithmetic Index with Column Temperature A—in Squalane

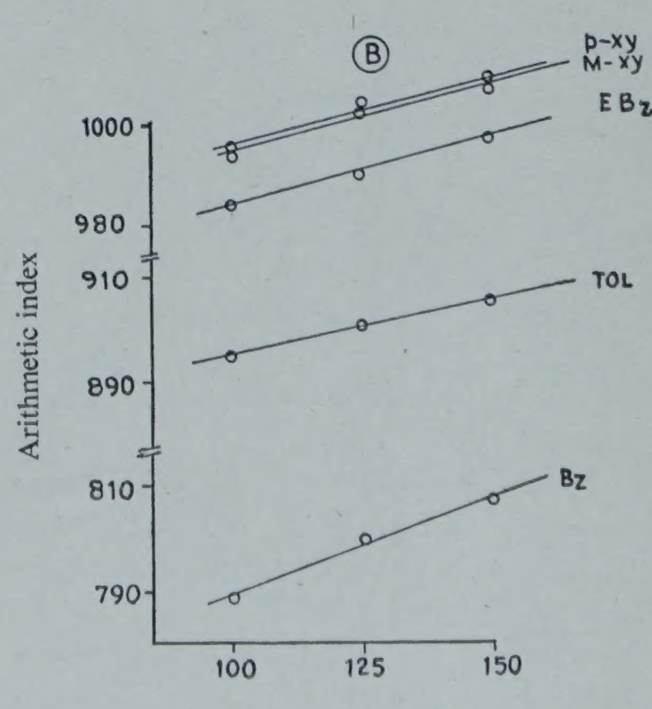


Fig. 3B—Linearity of Arithmetic Index with Column Temperature B—in Polypropylene Glycol

above application. Fig. 3 can be compared with the corresponding plots of references 8 and 17, where I has been used. I can be adequately substituted for I_A in determining other characteristics of retention index-temperature plots, such as in the selection of conditions for optimum resolution, in finding peak inversion and coelution temperatures. For the classification of hydrocarbons into chemical types with the help of the new parameter of temperature coefficient of index per unit carbon atom, it appears from Table 2 that arithmetic index is somewhat inferior to retention index. It can be noted (Table 3) that the index increment per degree column temperature is larger for arithmetic than for Kovats index for all compounds in a liquid phase, thereby indicating a stronger temperature dependence of I_A.

TABLE 2—Comparison of Temperature Coefficient of the Two Index Systems in the Classification of Hydrocarbons into Types in Squalane

Hydrocarbon Type	$\frac{UI/dT}{n} \times 10^3$	$\frac{dI_A/dT}{n} \times 10^3$
Monoalkyl	2-10	13-20
Dialkyl	6-18	19-33
Trialkyl	10-38	30-33
Cyclo-paraffins	30-38	31-46
Aromatics	45-58	44-60

TABLE 3—Comparison of the Temperature Dependence of Arithmetic and Kovats Retention Indices on Squalane

Compound	I/°C	I_A/°C
22 DMB	0.084	0.135
23 DMB	0.084	0.170
2 MP	0.017	0.051
CP	0.150	0.166
CH	0.233	0.316
Benzene	0.25	0.316
Heptene-2	0.00	0.000
Hexene-2	0.00	0.016

4.4. It has been demonstrated[18,22] that retention index can be determined with good accuracy by graphical methods. Arithmetic indices of a compound can also be obtained similarly (vide Fig. 4).

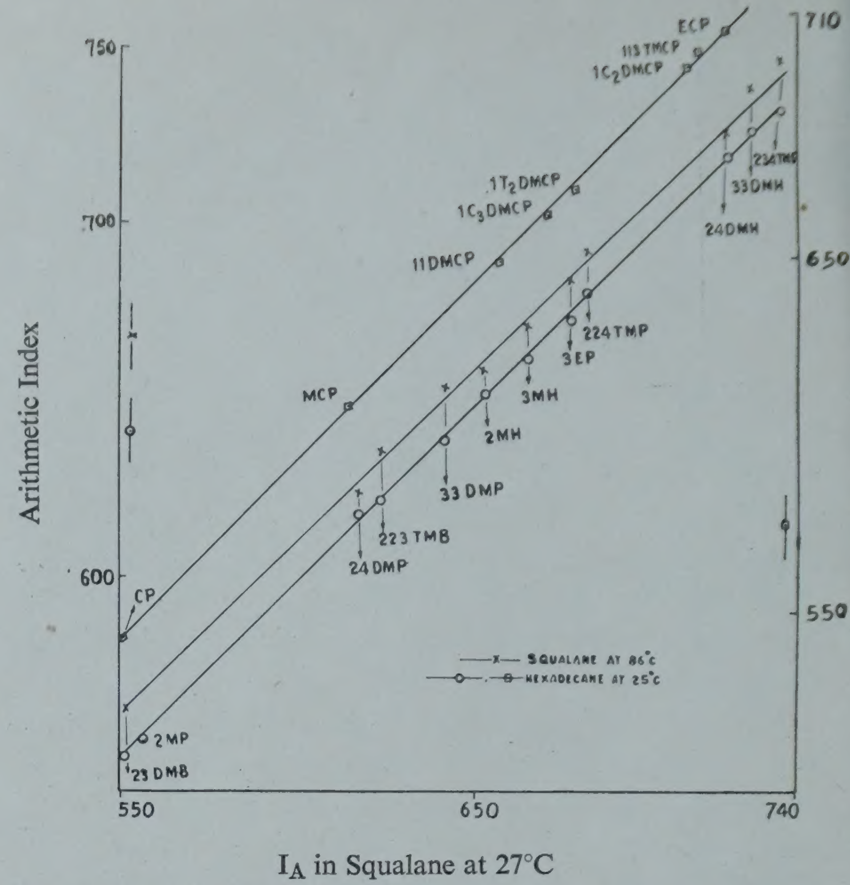


Fig. 4—Correlation of I_A of Solutes in Two Stationary Liquids at the Same Column Temperature and in the Same Stationary Liquid at Two Column Temperatures

5. Conversion of the Retention Index to Arithmetic Index

The above discussion shows that arithmetic index can replace retention index in most of its uses. Therefore, it would be necessary to convert existing retention indices in literature to corresponding I_A values. The following methods are proposed.

5.1. *From Graphical Correlations*: Fig. 5 shows that the points of the plot of (I—100 n) versus (I_A—100 n) lie on smooth curves. Such a plot will give a direct and fairly accurate interconversion of the two index systems. Fig. 5 was built up with a few properly chosen compounds, whose I and I_A values were determined experimentally. Such plots are independent of the nature of solutes and the range of normal paraffin pair, but dependent on stationary liquid and the temperature of the column. It will be clear from the following methods that the desired values of I and I_A can also be obtained graphically (vide Figs. 6A, 6B) without doing any fresh experiment. The underlying mathematics for graphical methods have been worked out for retention index[17] but not for arithmetic index.

5.2. *From Adjusted Retention Data of Normal Paraffins*: The method is based on strict linearity of logarithm of adjusted retention time, distance or volume of normal

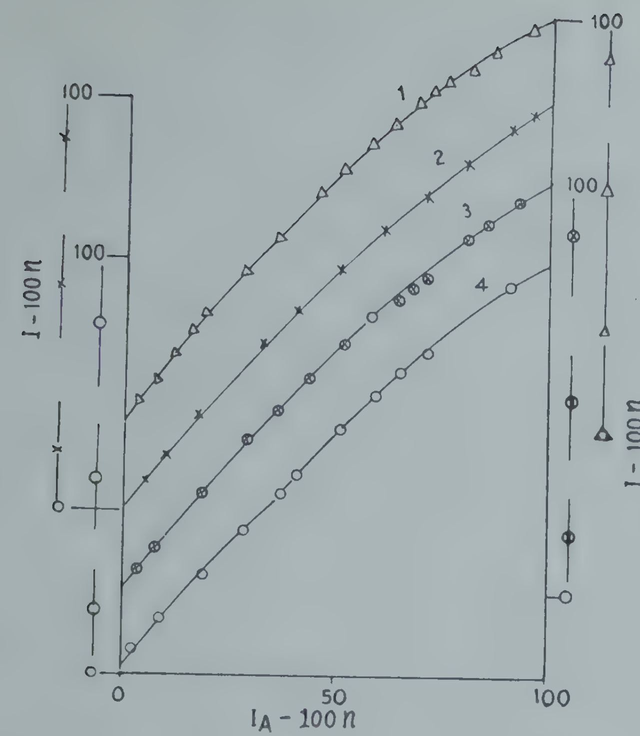
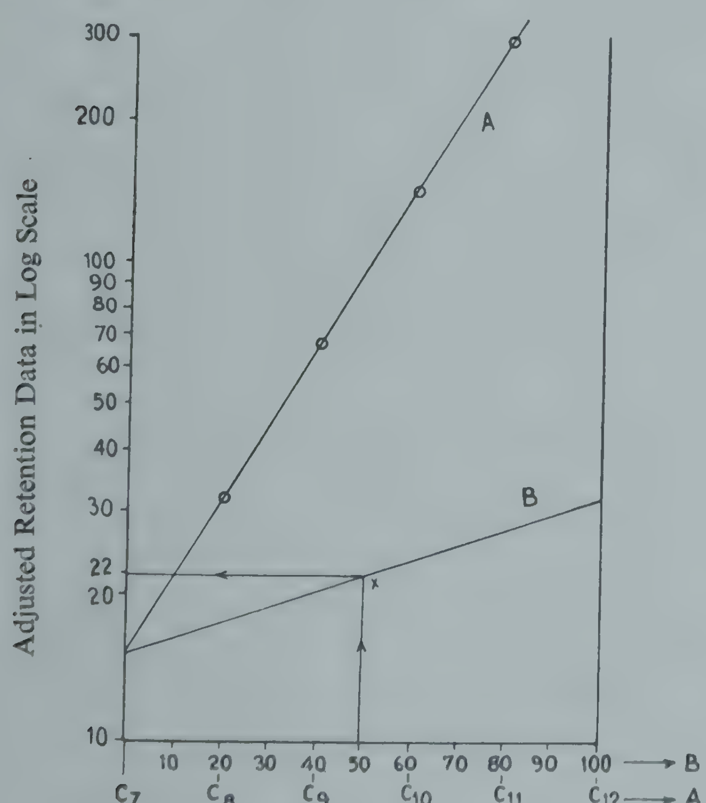


Fig. 5—Correlation of I and I_A Values for Hydrocarbons on Different Stationary Liquids at 80°C

1—Squalane
2—Dinonylphthalate
3—Dodecanol
4—Polyethylene Glycol

paraffins against their number of carbon atoms, in combination with the concept of nomographic methods for finding retention index, proposed by Hupe[22]. First of all, draw the straight line A (Fig. 6A) from three or more retention data of n-paraffins. Suppose, it is required to find the I_A value corresponding to retention index of 750 under the conditions of liquid phase and temperature given for line A in Fig. 6A. On the same semi-log graph, draw line B corresponding to the retention data (obtained from line A) of n-heptane and n-octane, the abscissa being divided into 100 equal index units. Find the ordinate of that point on line B whose abscissa, (I-100 n), is 50; this value, viz. 22 in this case gives the retention data of the compound. Then draw on a plain graph paper (Fig. 6B) the equivalent of line B (of Fig. 6A) corresponding to the same normal paraffin pair. The point on line C in Fig. 6B corresponding to the ordinate of 22 reads (I_A —100 n)= 41, i.e. the desired arithmetic index is 741.



B → I—100n
A → Carbon Number

Fig. 6A—Graphical Method of Conversion of I to I_A

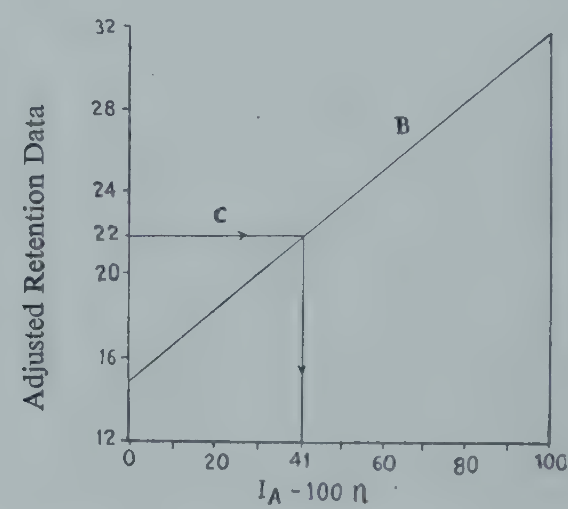


Fig. 6B—Graphical Method for Conversion of Retention to Arithmetic Index

5.3. *From Slope of Line, Log R_n V_s n*: Some gas chromatographers follow the practice of providing along with retention indices the value of the slope (S) of the straight line—logarithm of adjusted retention data R'_n against carbon number of n-paraffins. From the slope value, draw a line by assuming an arbitrary value of the adjusted retention data for the lower n-paraffin, the value of the next higher normal paraffin being fixed as $R'_n \log^{-1} S$. This straight line will be parallel to the actual line drawn with the help of absolute values of corrected retention data of the two n-paraffins. Then following the procedure described in the previous method one can easily convert I value to the corresponding I_A values.

When the slope in a stationary liquid is given for a temperature other than the desired one, the same can be obtained mathematically as derived from basic equations.

$$\text{Log } R'_n = \frac{-\Delta H}{RT} + C \quad (1)$$

$$\log R'_n = Sn + b \quad (2)$$

Where, R'_n = Corrected retention volume of a normal paraffin containing n carbon atoms.

$-\Delta H$ = Heat of solution, which may be taken as constant for a small variation in temp.

T = Column temperature, °K

R, S, b and C are constants.

$$\therefore \; Sn + b = \frac{-\Delta H}{RT} + C \qquad (3)$$

$$\text{or } Sn + b = \frac{m}{T} + C$$

$$\text{or } \; S = \frac{m'}{T} + C' \qquad (4)$$

Where, S is the desired slope of straight line in equation 2. The equation 4 was verified with a few stationary liquids in Fig. 7. A special mention may be made about

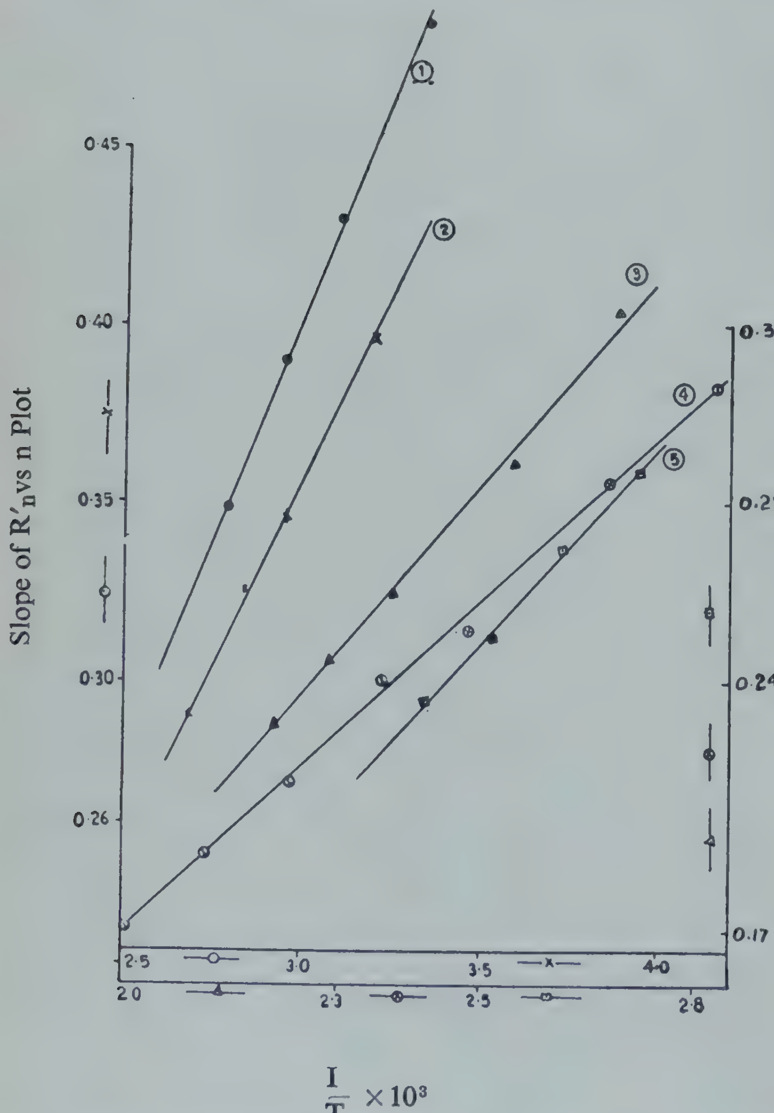


Fig. 7—Linearity of Slope of Equation 2 with Column Temperature
1—Squalane
2—Polypropylene, Glycol
3—Dioctyl Isoselacate
4—SE-30
5—High Vacuum Silicone Grease

SE-30, which gave a good linear fit, practically for its full working temperature range, i.e. from 30 to 200°C, thereby justifying the assumption of constancy of heat of solution with column temperature.

5.4 *From Chromatograms Containing a few n-Paraffins*: From the retention distances measured from injection points in the chromatographic trace—of four adjacent n-paraffins a linear plot, like that of Figs. 8A or 8B, is drawn. This provides uncorrected R_n values for all the n-paraffins required for the computation of I_A values

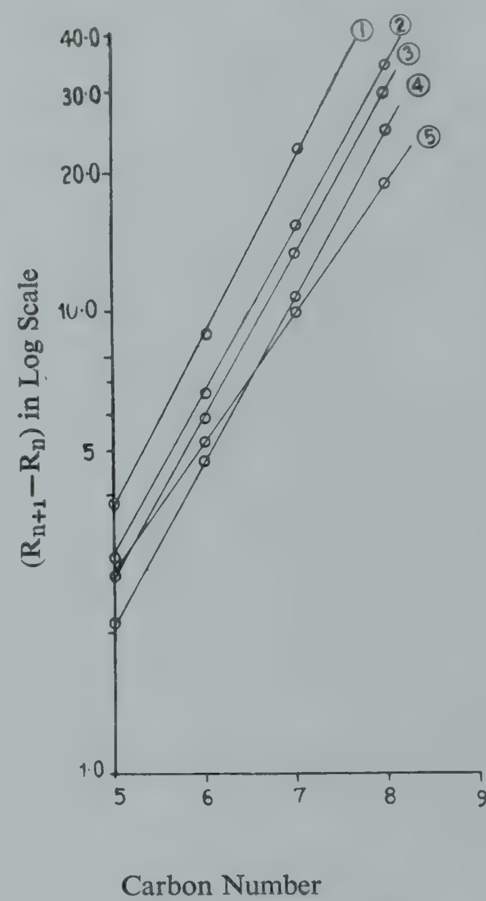


Fig. 8A—$(R_{n+1}-R_n)$ vs Plot in Different Liquids at 80°C
1—Squalane
2—Dodecanol
3—Dioctyl Sebacate
4—Dinonylphthalate
5—Polyethylene Glycol-400

of all peaks in the chromatogram. From the values of retention distance R_x of the peak X, and of R_n and R_n+1 (of the n-paraffin pair between which the compound in peak X elutes) thus obtained, the desired arithmetic index can be calculated from Harbourn's[20] formula, i.e.

$$I_A = 100\,n + 100\,\frac{R_x - R_n}{R_{n-1} - R_n} \qquad (5)$$

6. *Characteristics of* $(I-I_A)_{max}$: It has been noted that retention index is always greater than its corresponding arithmetic index; this is true for all solutes, stationary liquids and column temperatures. An examination of

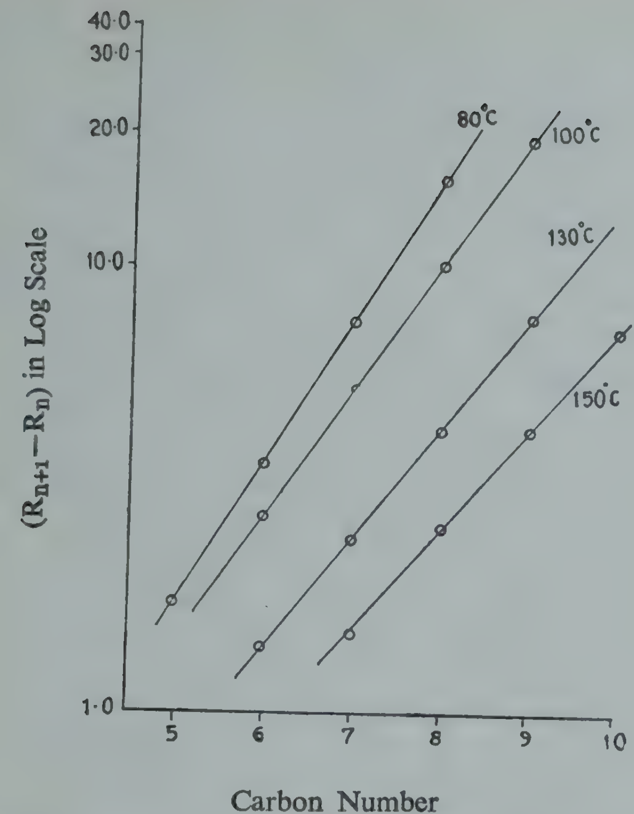


Fig. 8B—$(R_{n+1}-R_n)$ vs n Plot in SE-30 at Different Column Temperatures

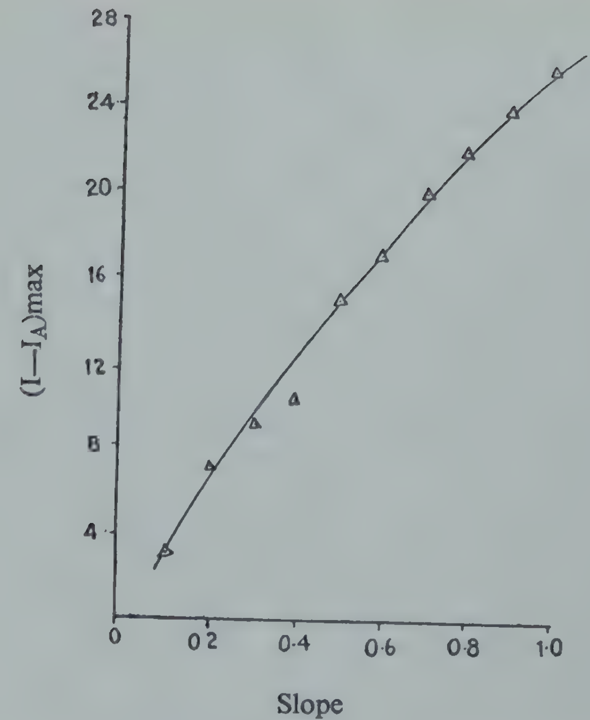


Fig. 10—Variation of $(I-I_A)_{max}$ with Slope of Equation 2

Fig. 5 reveals that the values and position of the maximum difference in the two indices depend on the nature of liquid. In addition, Fig. 9 shows the nature of variation of $(I-I_A)_{max}$ with column temperature.

On finer analysis, it has been found that $(I-I_A)_{max}$ is governed by the slope S of equation 2. It has been observed from our data as well as of others[31] that this slope is very strongly dependent on column temperature and slightly on the nature of stationary liquid (vide Fig. 8). In building up Fig. 10, I_A was caluclated for various values of I in the domain, $0 \leq (I-100\ n) \leq 100$ corresponding to any given slope value with the help of Figs. 6A & 6B.

From S values at 0°C for a large number of stationary liquids graphically determined from data of this laboratory and elsewhere[10,29], it has been observed that this slope is always less than 0.6, which implies that no stationary liquid can give $(I-I_A)_{max}$. greater than 18 as is evident from Fig. 10. This finding is also corroborated by the results in Fig. 9 for three liquid phases of different polarity. Our choice of 0°C was based on the fact that $(I-I_A)_{max}$. values increase with decreasing column temperature and also that very few stationary liquids are known to be efficient at temperatures below 0°C.

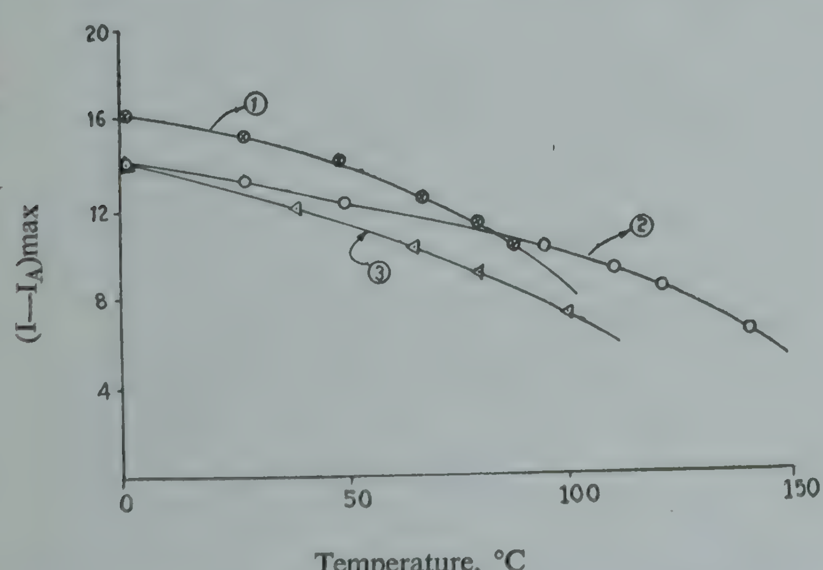


Fig. 9—Variation of $(I-I_A)$max with Column Temperature in Different Stationary Liquids

1—Squalane
2—High Vacuum Silicone Grease
3—Polypropylene Glycol

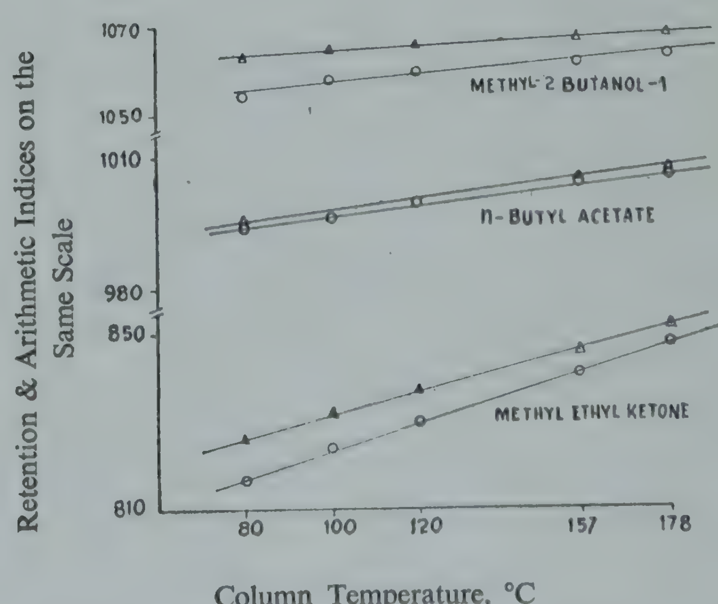
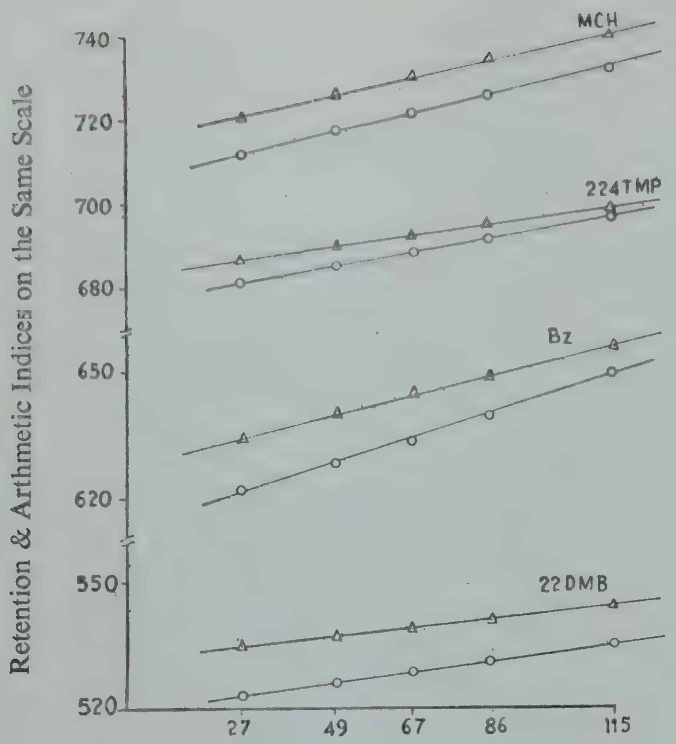


Fig. 11A—A Plot of Index Values Against Column Temperature in Neopentyl Glycol Adipate I in Upper Plot, I_A in Lower Plot



Column Temperature, °C

Fig. 11B—Similar Plot in Squalane is in Fig. 11A

Conclusion

Contrary to expectations—because of its apparently weak theoretical footing—the arithmetic index has been found to successfully substitute the Kovats retention index in most of its known uses in gas chromatography. This investigation justifies further research to enable choice of one index over the other or to ascertain whether both play complementary or supplementary role. In this context, it will be noted that when either of the index values is known for a compound the other is also fixed, because the slope of the straight line log R'_n V_s n becomes constant under the given set of conditions. It will definitely be a breakthrough in the problem of peak identification in gas chromatography (in other forms of chromatography also) if index value can be rigidly correlated with and predicted from the structures of solute molecules. It is believed that the two index systems—separately and jointly—as well as the $(I\text{-}I_A)_{max}$. parameter will find new significance in the accurate prediction of index value from considerations of structural features of solute and solvent molecules.

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ADDENDUM

The comments of the experts, named in acknowledgements section, being more or less of the same nature, have been generalized and included in the addendum along with the answers by the authors—**Editor.**

Comment: The appearance of arithmtic index (I_A) is unfortunate as it will divert the attention of the few researchers engaged on the application of index problem; hence the introduction and

application of I_A, primarily proposed by Harbourn is unnecessary.

Answer: The absence of logarithmic functions will result in faster calculation in I_A, as well as eliminate the use of gas hold-up time and accurate marking of injection point, which are the inherent sources of error with Kovats Index. In the computation of I_A, any arbitrarily fixed point on the recorder chart can be used as time of injection.

Comment: The calculation of I, can be made faster with additional aids, like (a) special logarithmic measure (b) nomograph (c) computer.

Answer: Since many gas chromatography laboratories do not have or cannot afford computer facility, which is the best gadget for this purpose, the simplified expression of I_A, will no doubt have its own field of application.

The I_A-T plot can be made almost instantaneously as the peaks are emerging in the recorder trace; this is not possible with retention index.

Comment: The ease of calculation and simplicity of the expression of I_A, cannot be taken as sufficient reasons in replacing I.

Answer: The objective of this paper is not to substitute I with I_A, but to recommend both the systems as complementary to one another.

As mentioned in the text, I_A, is equally satisfactory for most of the common uses of I. We hope that this paper, although apparently controversial in nature and contents, will stimulate further research and eventually bring out more and more of the potentialities of I_A, which cannot be fully seen at the present. Additionally, both the index systems can be gainfully utilised in other forms of chromatography, including gas-solid, thin layer, gel permeation, paper and liquid chromatography.

Comment: The concept of I_A, assumes unavoidable use of two paraffins, which are neighbours. This limitation makes I_A, less accurate, hence incapable of providing better system in identification of peaks.

Answer: We agree that the calculation of I_A is made from the retention data of two n-paraffins immediately preceding and succeeding the solute peak of interest. However this limitation can be removed to a great extent by using the uncorrected retention data of only 4 adjacent n-paraffins and plotting log $(R_{n+1}-R_n)$ Vs carbon number, as shown in Figs. 8A & 8B of the text.

From experience we find better reproducibility and accuracy in I_A values than I values, when both are calculated from the same set of corrected retention data. Using corrected or uncorrected retention distances measured from any arbitrary injection point same I_A values are obtained.

Therefore, I_A will give an equally good system, if not better, as the I system. In fact, plots similar to those in Figs. 1, 2, 3A and 3B of the text reveal no significant difference in data fitness of the two index systems.

It is known that in the case of retention index the primary standards of n-paraffins can be replaced with suitable secondary standards, like, benzene, toluene, ethylbenzene, n-propyl benzene etc. for aromatic hydrocarbons. Similar is the status of arithmetic index as has been found in this laboratory.

Comment: I_A, is divorced from correlation with standardised retention data and thermodynamic functions unlike retention index.

Answer: It has been elaborated in the text that the two index systems are quantitatively inter-convertible. Hence, at least indirectly, I_A can have benefit of correlations with other known retention and thermodynamic data via Kovats index, although the former is, per se. devoid of thermodynamic footing.

Comment: I Vs I_A plot is not linear, so if a plot is linear with one index it cannot be so in the other.

Answer: The linearity of I_A or I with column temperature is an experimental fact, (vide Figs. 10 A & B). A critical examination of data scatter in these plots reveals no significant difference or preference of the two systems. An additional point is that the periodic nature of I Vs I_A plot in Fig. 5 of the text, can be approximated by a linear fit, particularly for the region of (I-100 N), or (I_A-100 N) lying in the domain of 20 to 80 index units. The scatter of data in such plots seldom exceeds $\pm$ 2 index units.

Comment: The I-T linearity is valid for a limited temperature interval, and varies with nature of solute-solvent pairs. The same problems remain with I_A-T plot. The linearity region generally terminates in the vicinity of highest working temperature of the stationary liquid.

Answer: From critical analysis of massive data from literature and our own experiments, it has been established that the rule of I-T or I_A-T linearity is valid upto the full thermal range of stationary liquids and for all possible combinations of solute-solvent polarity. A detailed report on this topic will be published soon. It has been observed that the degree of accuracy in data fitness is somewhat inferior, when polarity difference in solute-solvent is very high. Moreover, an apparent deviation of linearity rule (particularly at higher column temps.) can often be noted with solute having high temperature co-efficient of index. This may be attributed to possible inaccuracy of recorded temperature and other measuring errors.

Comment: The concept and contents of Harbourn's formula and that of Van Den Dool and Kratz are not equivalent. By linear interpolation one gets PTGC index from isothermal I values. This is something not possible with the I_A system.

Answer: A similarity in the expression of the I_A and in the correlational formula of PTGC and isothermal I, can be noted. Of course this is purely incidental. The relation of isothermal and PTGC arithmetic index has not been investigated and hence is beyond the scope of this paper.

[Original mss. received on July 11, 1970]

The changes which occur on grinding a reformation catalyst are primarily of sub-division of larger particles resulting in an increase in the specific surface area, apparent density and formation of finer pores followed by on further grinding a secondary process of agglomeration, which causes reversal of the acquired physical properties. These changes have been compared with those taking place during the heat treatment process. Hydrogen reduction of ground and heat-treated samples has been examined and it has been shown that resistance to hydrogen reduction offered by heat-treated samples in due to the formation of nickel aluminate ($NiAl_2O_4$) at higher temperature.

Effect of Mechanical & Heat Treatment Processes On Physico-Chemical Properties of Reformation Catalyst

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The methods of preparation and pretreatment steps during the manufacturing stage of catalysts greatly influence the structure and catalytic activity of the finished product. Grinding is one of the many such processes, known to have pronounced effects on the reactivity of solids. Papmahl[1] *et al* have studied the effect of grinding on nickel-kieselguhr catalyst. The catalytic activity of metallic catalyst[2] has been shown to increase with grinding. When solid materials are subjected to crushing or grinding, apart from a change in surface texture, particle shape and size, their physical and chemical properties also undergo a change[3]. Different workers[4-8] have studied the physico-chemical properties of nickel oxide, zinc oxide and alumina with respect to grinding periods. Reduction temperatures of the oxides of iron, nickel and copper, etc. are reported to be lowered[9] by 40-150°C on grinding. Whereas the effect of mechanical treatment has been studied for several oxides, less attention has been paid towards industrial catalysts having more than one component.

In the present investigation, the effect of mechanical and heat treatments on the physico-chemical properties of nickel oxide-aluminium oxide (NiO-Al_2O_3) type reformation catalyst has been studied. Behaviour towards hydrogen reduction has also been examined and compared with the changes imparted by heat treatment of the samples.

Experimental

Catalyst Preparation: The catalyst samples were prepared by co-precipitation with ammonium carbonate, from a suspension of alumina powder in nickel nitrate solution. The precipitate was filtered, washed and dried at 120°C. The alumina used for coprecipitation was mainly α-alumina with γ-alumina as minor phase. Two different series of samples were prepared from the dried precipitate.

Series A—The dried precipitate was dry ground in a ball mill and samples were collected at different intervals of time. The samples were cured at 450°C before making various studies to ensure that nickel salt is completely decomposed to NiO. The chemical analysis indicated 7.6 per cent of nickel in the samples.

Series B—The dried precipitate was initially ground for 16 hr. Aliquots of ground catalyst samples were then heat-treated at different temperatures in the range of 450-950°C.

Measurement of Surface Area, Pore Volume, Pore Size Distribution and Particle Size: The surface areas were determined by the BET low temperature nitrogen adsorption method and pore volume and particle size, etc. as described in an earlier publication[10].

Pore size distribution was determined by mercury penetration method using an Aminco-Winslow poro-

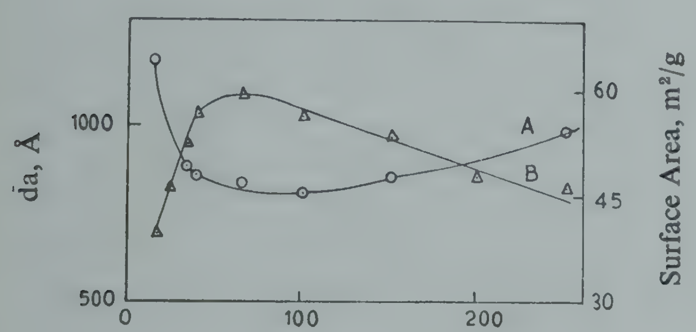
simeter having a working pressure range upto 15000 lbs/sq. inch.

Hydrogen Reduction: The reduction studies were carried out in a Stanton thermobalance* with a sensitivity of 0.2 mg./div. A steady flow rate of 1.5 lit./hr. of hydrogen was maintained during the reduction periods. Isothermal reduction at 450°C and initiation of reduction temperature by heating the sample in an atmosphere of hydrogen were studied.

Results and Discussion

Specific Surface Area, Particle Size and Porosity

A. *Effect of Grinding*: The specific surface areas and the average particle sizes of the catalyst samples are plotted against the grinding periods (Fig. 1). The specific



Grinding time, hr

Fig. 1—Changes in Surface Area and Particle Size with Grinding

A—$\bar{d}a$, Average Particle Diameter
B—Surface Area

surface area increases sharply during the initial grinding, reaching a maximum at about 65 hours grinding. This may be due to the primary process of formation of finer particles. Beyond 65 hr. the surface area decreases slowly which may be attributed to the formation of secondary particles which grow due to the agglomeration of primary particles. The changes in the surface area values are supported by the study of the average particle size wherein there is first a gradual decrease in the particle size due to the formation of finer primary particles. After about 100 hours grinding, the particle size again increases which may be attributed to the process of agglomeration of finer particles at this stage. The effect of grinding on surface area in the first 30-40 hr. of grinding is, in fact, maximum indicating the limit of the mechanical forces in the ball mill to break the original larger particles. Thus, only the primary structural changes in the reformation catalyst greatly contribute to an increase in the surface area, while the secondary effects are not very much pronounced, since decrease due to secondary process is slow. In any case the specific surface area does not approach a constant value within the period under investigation, and that a maximum point is reached at 65 hours. This effect is similar to that observed by Gregg for graphite and kaolinite[11].

The true densities as determined by helium displacement (Table 1) remain almost the same, but changes in apparent density are considerable up to certain period of grinding. The pore structure of the ground samples are represented in Fig. 2. It is apparent from the figure that the changes take place only in the smaller pores of upto 500Å radius. Upto a grinding period of 65 hr. percentage of smaller pores increases as a result of grinding till the stage of agglomeration. These changes in the pore structure of the catalyst with grinding account for the sharp increase followed by gradual decrease in the specific surface area.

TABLE 1—True and Apparent Densities and Corresponding Pore Volumes after Grinding

Grinding Period, hr.	True Density, g./cc.	Apparent Density, g./cc.	Total Pore Volume, cc./g
16	3.85	1.30	0.51
34	3.89	1.29	0.52
40	3.86	1·23	0.55
65	3.91	1.21	0.57
100	3.95	1.31	0.51
150	3.87	1.31	0.50
200	3.91	1.31	0.50
250	3.92	1.30	0.51

Thus, it can be seen that changes which occur during the grinding periods in reformation catalyst are primarily of subdivision of larger particles resulting in more of the exposed surface, increase in apparent densities and formation of finer pores followed by secondary process of agglomeration which causes reversal of the acquired physical and structural properties, the latter effects being comparatively much slower. No periodical change has been observed in the properties on grinding as observed in the case of sodium chloride[12].

B. *Effect of Heat Treatment*: For a comparative study of heat treatment and mechanical treatment processes, the properties of heat-treated samples were similarly studied. The specific surface area and particle size

* Model MF H-5, Mass Flow Type

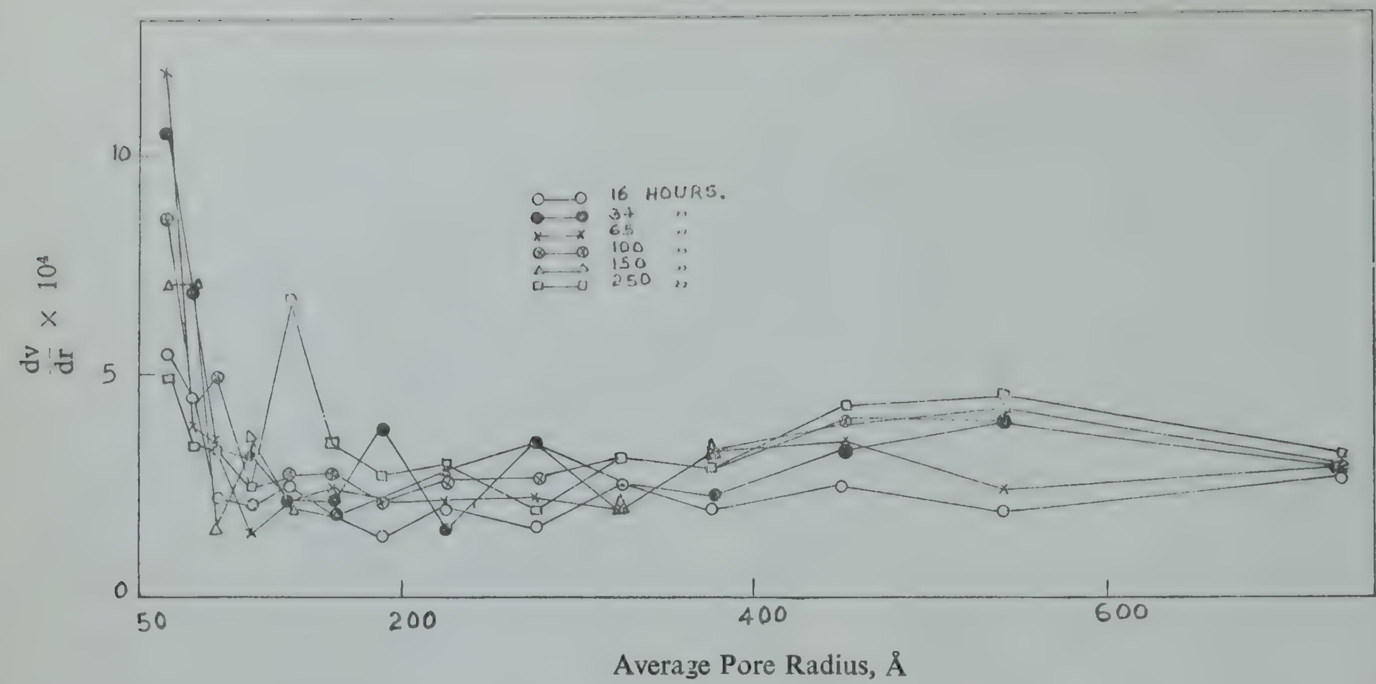


Fig. 2—Distribution of Pores in the Ground Samples

against temperature are plotted in Fig. 3. The pore size distribution curves are given in Fig. 4, while Table 2 gives the result for true and apparent densities along with the corresponding pore volumes.

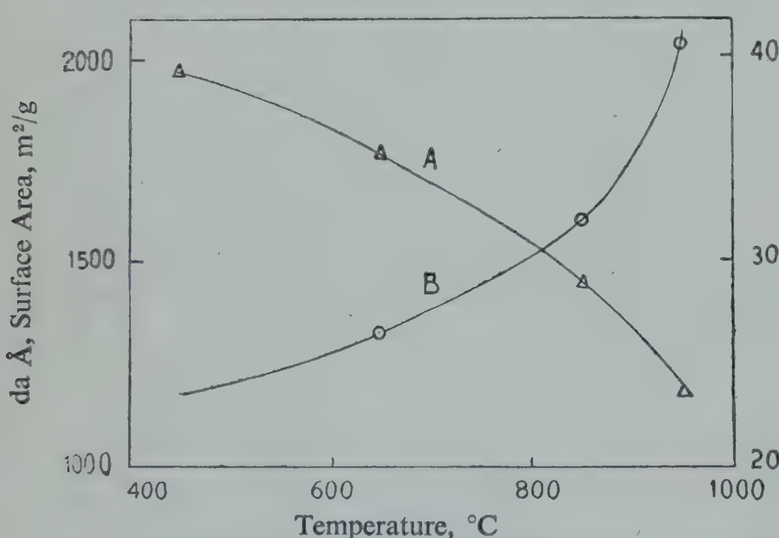


Fig. 3—Changes in the Surface Area and Particle Size with Curing Temperature
A—Surface Area
B—da, Average Particle Size

TABLE 2—True and Apparent Densities with Corresponding Pore Volumes of Heat Treated Samples

Curing Temp., °C	True Density, g./cc.	Apparent Density, g./cc.	Total Pore Volume, cc./g.
450	3.85	1.30	0.51
650	3.95	1.30	0.51
850	4.00	1.30	0.51
950	3.85	1.15	0.51

The specific surface area decreases with the increasing temperature in the range studied. The porous structure of the catalyst upto the pore radius of 500 Å is affected resulting in the gradual disappearance of smaller pores. This change is due to heat tratment resulting in an increase in particle size. These changes are comparable to one observed with the grinding for longer periods.

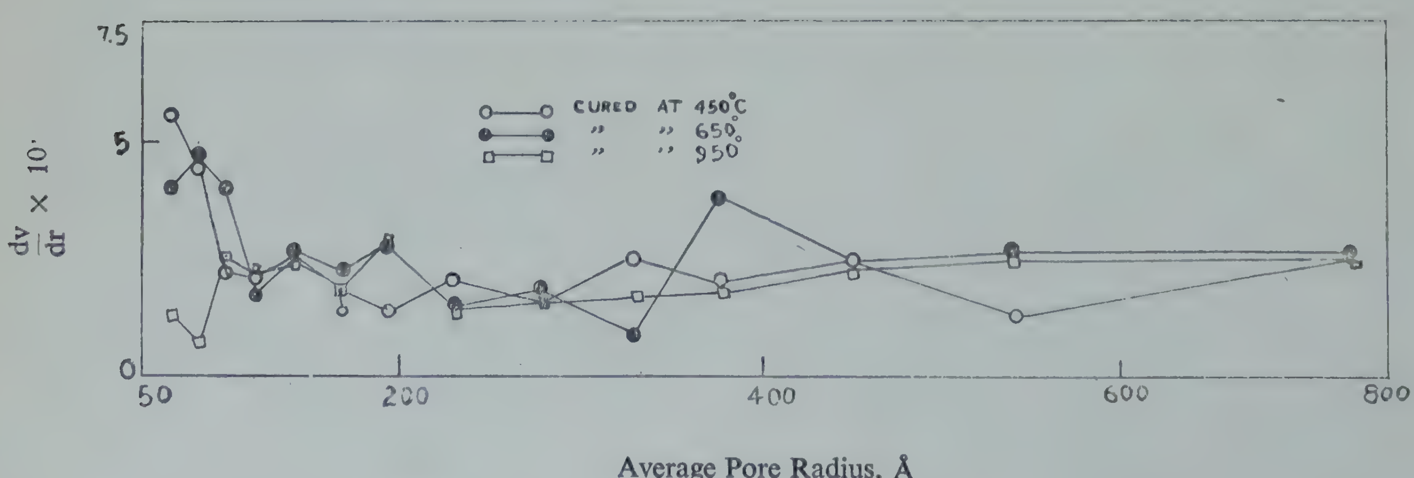


Fig. 4—Distribution of Pores in the Cured Sample

From the above observations, it can be concluded that the grinding of reformation catalyst for longer periods imparts similar changes in the physico-chemical properties as by heat treatment, the only difference being that changes due to the latter are more drastic.

X-ray results (Table 3) indicate the formation of the spinel, nickel aluminate ($NiAl_2O_4$), in the heat-treated samples. Sample heated at 850°C represents the formation of aluminate and in the sample cured at 950°C, whole of the nickel forms aluminate and no nickel oxide phase has been reported. In the case of ground samples, however, there is no formation of nickel aluminate.

TABLE 3—X-RAY DATA

Curing Temperature, °C	Phases Present
450	α—Al_2O_3, γ—Al_2O_3, NiO
650	α—Al_2O_3, γ—Al_2O_3, NiO
850	α—Al_2O_3, $NiAl_2O_4$, γ—Al_2O_3, NiO
950	α—Al_2O_3, $NiAl_2O_4$, γ—Al_2O_3

Hydrogen Reduction

Hydrogen reduction of nickel oxide on alumina had been the subject of much investigations and it is now believed that the rates and extent to which nickel oxide in the catalyst can be reduced is a function of distribution of nickel on the support[13-14]. The distribution of nickel on the support may as well be dependent on mechanical treatment or heat treatment of the catalyst. Hydrogen reduction rates of these samples were studied in order to see the effect of grinding or heating on the distribution of nickel.

The results of isothermal reduction of ground samples are shown in Fig. 5. At 450°C in all the samples nearly 60 to 65 per cent reduction takes place in 140 min. There appears to be no definite relationship between the grinding time and the total amount of nickel reduced in 140 min. This is not unexpected since the samples were prepared by coprecipitation method in which already a fine distribution of nickel is anticipated, mechanical treatment for the periods under investigation appears to have little or no effect.

The samples were heated in an atmosphere of hydrogen to study the effect of grinding on initiation temperatures for the reduction. Fig. 7 indicates such a relationship from which it can be seen that the reduction temperatures are gradually lowered to some extent and after 100 hr. of grinding become more or less constant. These results are similar to those obtained by Naiser *et al*[9].

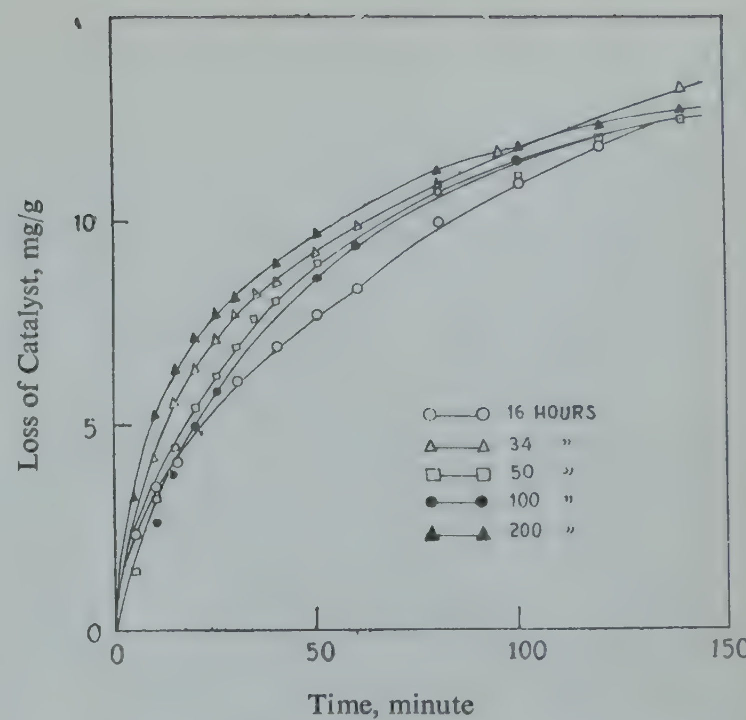


Fig. 5—Change in the Rate of Reduction with Grinding

Isothermal reduction at 450°C for the heat-treated samples are given in Fig. 6. It is to be observed that total amount of nickel which can be reduced at 450°C decreased with the increasing temperature of curing. In the case of sample heated at 950°C, there appears to be practically no reduction at all. This indicates that nickel

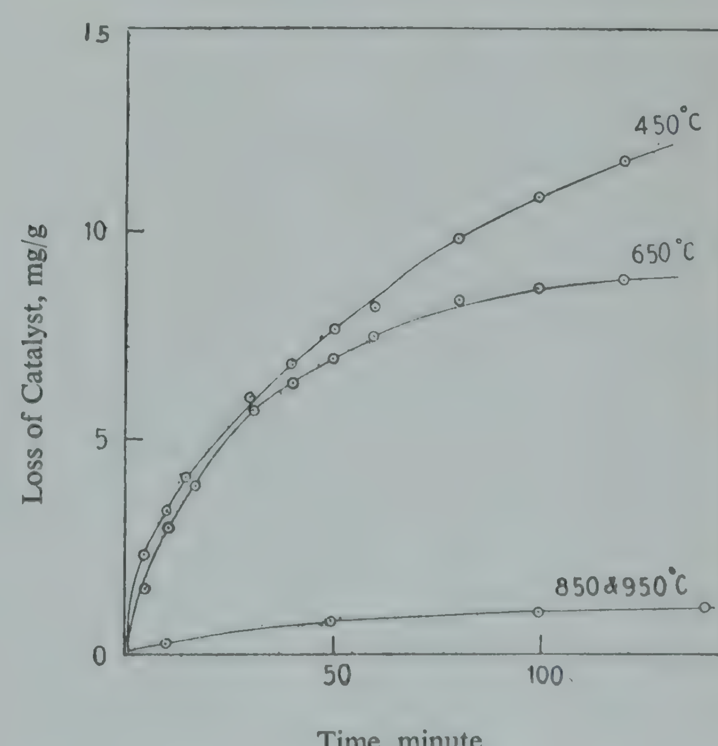
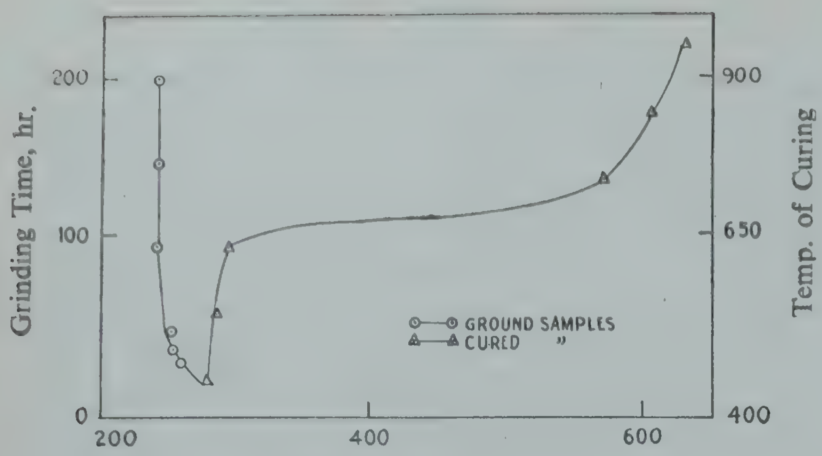


Fig. 6—Change in the Rate of Reduction with Curing



Temperature of Initiation of Reduction, °C

Fig. 7—Changes in the Temperature of Initiation of Reduction with Grinding and Curing

is gradually being transformed into such a type which is difficult to reduce. X-ray investigation has indicated the formation of nickel aluminate ($NiAl_2O_4$) at higher temperatures. From this it can be assumed that resistance to reduction offered by samples heated at higher temperature is due to nickel aluminate formation.

The temperatures at which reduction begins are plotted against temperature of curing in Fig. 7. With increasing temperature of curing, nickel combines with alumina to form nickel aluminate and thus the temperature at which reduction begins increases. In the sample cured at 950°C, the reduction commences at 650°C indicating that $NiAl_2O_4$ can only be reduced at or above this temperature.

Acknowledgements

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Five varieties of commercial catalysts have been studied to evaluate their specific catalytic activity for reformation of methane in presence of steam alone and also steam and oxygen together. The oxidation potential in terms of oxygen moles per mole of feed gas was kept constant at 0.75 in both the series. It appears that the catalytic activity is influenced to a great extent by the nickel content of the catalyst. There are exceptions to this observation which have been attributed to factors like method of preparation, composition and other physical parameters. Method of preparation being the same activity increases with increasing nickel concentration but specific activity (activity/sp. surface area) follows a reverse order. None of the catalysts show any specificity towards any of the methane-steam and methane-steam-oxygen reactions under the experimental conditions studied.

Catalytic Reformation of Methane

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Introduction

Natural, refinery and coke oven gas are widely used as raw materials, for manufacture of hydrogen. Hydrocarbons present in those gases react with steam at high temperature yielding hydrogen and oxides of carbon as below.

$$CnHm + nH_2O \rightarrow n\,CO + (n + \frac{m}{2})\,H_2 \qquad (1)$$

Reaction (1) represents hydrocarbon—steam reformation in general and is highly endothermic. In the above reaction higher the value of n i.e., higher is the number of carbon atoms per molecule of the hydrocarbon more will be the requirement of steam and chances of carbon liberation. Further, the CO produced by reaction (1) will react with additional quantity of steam forming CO_2 and hydrogen as below.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

Reaction (2) is exothermic and takes place simultaneously with reaction (1) in all hydrocarbon steam reformation processes. As the endothermicity of reaction (1) is much higher than exothermicity of reaction (2) the overall hydrocarbon steam reformation process still remains a highly endothermic one, and as such is favoured at comparatively higher temperatures. The product gas from these reactions will contain CO, CO_2, H_2 and unreacted methane and steam. The partial pressures of these components in the product gas depend on the reaction conditions such as steam to carbon ratio in the feed stream, temperature, pressure, contact time and efficiency of the catalyst used.

For the production of synthesis gas suitable for methanol, reformation of hydrocarbon is usually carried out in presence of steam alone in a single step at comparatively higher temperatures and lower pressures so as to bring down the unreacted methane content to a very low level. But in case of synthesis gas for ammonia where nitrogen is to be incorporated in the process gas the reformation is carried out in two stages. In the primary reformation stage the hydrocarbon reacts with steam at a comparatively lower temperature producing a gas containing 6-10 per cent unreacted methane. In the second stage calculated quantity of air is dosed into the secondary reformer top so as to buildup desired nitrogen concentration in the synthesis gas. Introduction of air into the secondary reformer liberates considerable heat due to combustion thereby attaining a high temperature at the secondary reformer top. Due to high operating temperature of the secondary reformer it is possible to get a reformed gas with very low methane content at the secondary reformer exit.

Hydrocarbon reformation is also carried out some time in autothermal reactors where both steam and oxygen or enriched air are introduced along with hydrocarbon gas. Presence of oxygen in the feed stream eliminates necessity of supplying heat from external source.

The catalytic reformation of methane in presence of steam alone or steam and oxygen has been studied by many workers[1–10] and a number of patents[11–24] for the processes and catalysts are available in the literature. The reaction between methane and steam, which is a specific case for reaction (1), takes place as follows.

$$CH_4 + H_2O \rightarrow CO + 3H_2 + 49.3 \text{ K Cal} \quad (3)$$
$$CO + H_2O \rightarrow CO_2 + H_2 - 9.8 \text{ K Cal} \quad (4)$$

In an autothermal system or in the second stage of two stage reformation where oxygen is introduced along with feed gas the following reactions will also take place in addition to methane-steam and shift reactions.

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \quad (5)$$
$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2 \quad (6)$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (7)$$

Reactions 5, 6 and 7 are exothermic and supply necessary heat for methane steam reaction in autothermal and secondary reformation process.

The primary reformation is an endothermic process and requires external supply of heat. The temperature of the product gas at the exit of primary reformer is normally maintained between 700°C and 800°C. The temperature in the secondary reformer is generally very high due to the heat generated from the exothermic reactions between oxygen and process gas, which ranges between 950°C and 1050°C and sometimes still higher at the inlet side and 860°C and 920°C at the exit side. Single stage autothermal reformers are generally operated with a bed temperature of 800°C to 1000°C and the exit gas temperature of 750°C to 800°C.

From the foregoing discussions it appears that the service requirements of the reformation catalyst in primary, secondary and autothermal reformation will be different in view of the difference in process conditions. Primary reformation catalyst needs to be more reactive at lower temperatures and should resist carbon liberation. On the other hand secondary reformation catalysts have to function at comparatively higher temperatures and higher throughput of gas. At higher temperatures chances of deactivation by sintering and nickel depletion from surface are more and the catalyst must be suitable to resist it. In the autothermal reformation process the catalyst probably should possess the properties to suit the service conditions of both primary and secondary reformation processes.

In consideration of the above, it may be appropriate to recommend specific type of catalyst for particular service condition. But necessary data supporting this view are not available. In the present investigation five catalysts were studied to evaluate their catalytic activity in presence of both steam alone and steam and oxygen together. Total oxidation potential in terms of oxygen in the feed was maintained same in both the type of reactions. Out of the five catalysts used in this investigation two have commercial application in primary reformation, one in secondary reformation and the remaining two along with the third one in autothermal reformation. Selection of temperature in the present series of experiments is somewhat a compromise between primary and secondary reformation condition.

Experimental

Altogether five catalysts of different makes, which are already in commercial use have been chosen for the present investigation. The details of those samples are given in Table 1. Out of these, the catalysts designated as A and B are of two different makes while the catalysts C, D and E are all of the same make which is different

TABLE 1—Chemical Composition (% by wt.) and Surface Area

Catalyst	A	B	C	D	E
Loss on Ignition at 900°C	11.7	18.9	2.10	1.81	2.26
SiO_2	—	13.75	—	—	—
Al_2O_3	47.30	18.80	85.01	91.60	94.24
Fe_2O_3	—	5.44	—	—	—
NiO	35.12	23.25	12.80	6.36	3.21
CaO	5.90	7.80	—	—	—
Mgo	—	11.74	—	—	—
Specific Surface Area, m^2/g.	31.8	76.3	47.5	39.6	36.5

from that of A and B. Catalysts A and B have commercial use in primary reformation of methane in presence of steam alone. Catalyst C has industrial application as a secondary reformation catalyst and catalysts D and E are being employed along with catalyst C in autothermal reformation of hydrocarbon fractions of coke oven gas, containing mainly methane.

The specific surface area of each of these catalysts in unreduced condition as shown in Table 1, was determined by BET method.

For activity tests a bench scale unit identical to the one described in some of the authors' previous work[10] was used. A provision was made in the testing unit to feed measured quantity of oxygen at the point where the hydrocarbon steam mixture entered the preheater. All experiments are carried out under atmospheric pressure.

The feed gas used for the experiments was the fraction of coke oven gas consisting mainly of methane (60 to 70 per cent) obtained directly from gas reforming plant of Sindri Fertilizer Factory. 100 cc of each of the catalyst samples was charged in turn in the reactor. The temperatures of saturator, preheater and reactor were gradually raised with flow of nitrogen through the system. When the temperatures of the preheater and reactor reached 600°C and 800°C respectively and the saturator temperature was well above the desired saturation temperature, hydrocarbon gas was slowly opened to the system through the saturator and nitrogen was cut off. During this initial period when the catalyst reduction took place the steam to gas ratio (by volume) was maintained at about 2. Reduction of catalyst usually took 2 to 3 hours' time after which the system was allowed to attain steady state with the desired conditions of experiment. Observing steady conditions for at least 2 hours, both inlet and outlet gas samples were collected simultaneously for analysis. The gas samples were analysed in an Orsat apparatus. Collection of samples under each reaction condition and analysis were repeated to ensure a steady condition. The activity results were calculated in terms of percentage of methane reformed.

Results and Discussion

In all the experiments of the present investigation the temperatures of the preheater and reactor were maintained constant at 600°C and 850°C respectively. Two sets of experiments have been carried out with each sample of catalyst, one in presence of steam alone and the other in presence of both steam and oxygen. For evaluation of comparative activity in presence of steam alone, steam to dry feed gas ratio was kept fixed at 1.5. When oxygen was introduced along with steam both steam to dry feed gas and oxygen to dry feed gas ratios were kept fixed at 0.5. Thus, in all experiments total oxidation potential in the form of either steam alone or steam and free oxygen was maintained constant at 0.75 mole of oxygen per mole of dry feed gas.

In the experiments carried out with steam alone the space velocity in terms of dry feed gas was varied between 400 and 1000. The results of these experiments have been shown in Table 2. For comparative activity percentage of methane reformed has been taken into consideration.

The experiments with both steam and oxygen were also carried out varying the space velocity between 400 and 1000 and the results have been shown in Table 3.

Chemical Composition and Specific Surface: It can be seen from Table 1 that on the basis of composition the five catalyst samples can be classified in three groups. Thus, catalyst A contains calcium oxide in addition to alumina and nickel oxide whereas catalyst B contains many components like oxides of calcium, iron, magnesium and silicon in addition to alumina and nickel. Catalysts C, D and E form a distinctly separate group which are alumina based nickel catalysts having no other component and containing comparatively much less nickel. Losses on ignition at 900°C are also much less in case of samples C, D and E.

On comparing the surface areas of the catalyst samples as shown in Table 1 it is observed that catalyst B is having the highest surface area and catalysts C, D, E and A are having surface areas in decreasing order. Specific surface areas of samples have been plotted against their corresponding nickel content in Fig. 1. It may be seen from this curve that specific surface increases with increasing nickel content so far as catalysts B, C, D and E are concerned. But similar relationship does not hold in case of catalyst A which having highest nickel content, possesses lowest specific surface area. Probably it is not the chemical composition alone but the method of preparation of the support material as well as the method of incorporation of active components which also determine the pore geometry and hence the specific surface of the finished product.

Activity in Presence of Steam: For comparison of activity of the different catalysts in presence of steam alone, the values corresponding to 800 space velocity have been taken into consideration. Curve A of Fig. 2 shows the relationship between activity and nickel content of the catalysts. Curve B of Fig. 2 shows the relationship of specific activity with nickel content.

Table 2—Activity Results of Steam-Methane Reactions

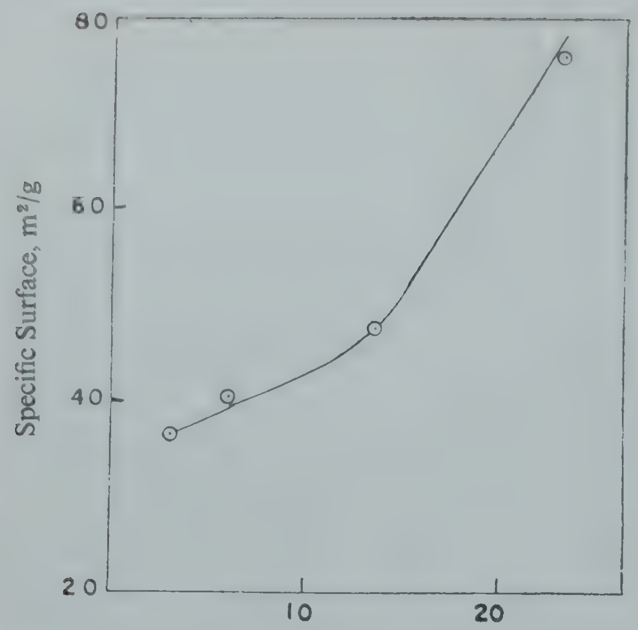
[Preheat Temp. 600°C, Reactor Temp. 850°C, Steam/Gas Ratio 1.5, Oxygen-to-Gas ratio nil]

Catalyst	Space velocity		Gas Composition, % by vol.							Conversion of CH_4, %
			CO_2	O_2	CnHm	CO	H_2	CH_4	N_2	
A	400	Inlet	Nil	1.0	7.4	11.2	2.0	70.2	8.2	94.5
		Outlet	3.0	Nil	Nil	27.0	65.8	1.2	3.0	
	600	Inlet	Nil	0.8	7.4	11.0	3.0	67.2	9.6	92.5
		Outlet	3.2	Nil	Nil	25.8	65.8	1.6	3.6	
	800	Inlet	Nil	0.8	8.4	10.4	3.0	68.2	9.2	91.6
		Outlet	5.0	Nil	Nil	24.6	64.8	1.8	3.8	
	1000	Inlet	Nil	0.8	8.2	10.0	3.0	68.4	9.6	90.0
		Outlet	6.2	Nil	Nil	20.4	67.2	2.2	4.0	
B	400	Inlet	Nil	0.8	7.2	11.6	3.2	66.8	10.4	92.9
		Outlet	4.0	Nil	Nil	25.6	66.0	1.4	3.0	
	600	Inlet	Nil	0.8	7.2	11.6	3.2	66.8	10.4	89.9
		Outlet	4.6	Nil	Nil	24.8	65.6	1.8	3.2	
	800	Inlet	Nil	0.8	7.6	9.6	3.0	69.2	9.8	86.4
		Outlet	5.0	Nil	Nil	23.6	64.6	3.0	3.8	
	1000	Inlet	Nil	0.8	7.6	9.6	3.0	69.2	9.8	83.9
		Outlet	6.6	Nil	Nil	21.4	64.0	3.8	4.2	
C	400	Inlet	Nil	0.8	7.6	9.8	2.8	69.6	9.4	92.3
		Outlet	3.8	Nil	Nil	25.8	65.6	1.8	3.0	
	600	Inlet	Nil	0.6	8.2	9.0	2.6	70.0	9.6	90.9
		Outlet	4.0	Nil	Nil	25.8	65.2	2.0	3.0	
	800	Inlet	Nil	0.6	8.2	9.0	2.6	70.0	9.6	87.9
		Outlet	4.0	Nil	Nil	24.0	65.8	2.6	3.6	
	1000	Inlet	Nil	1.0	8.2	9.8	2.8	68.4	9.8	85.1
		Outlet	4.0	Nil	Nil	24.0	65.2	3.0	3.8	
D	400	Inlet	Nil	1.0	9.2	11.4	2.8	64.6	11.0	91.0
		Outlet	4.0	Nil	Nil	24.8	65.2	1.8	4.2	
	600	Inlet	Nil	1.0	9.2	11.4	2.8	64.6	11.0	88.9
		Outlet	5.4	Nil	Nil	22.8	65.2	2.2	4.4	
	800	Inlet	Nil	1.0	7.8	11.2	3.4	66.2	10.4	85.5
		Outlet	6.2	Nil	Nil	21.6	64.8	3.2	4.2	
	1000	Inlet	Nil	1.0	7.8	11.2	3.4	66.2	10.4	82.4
		Outlet	6.4	Nil	Nil	21.0	63.8	4.0	4.8	
E	400	Inlet	Nil	0.8	8.0	10.0	3.0	68.4	9.8	90.4
		Outlet	3.8	Nil	Nil	25.4	66.2	2.0	2.6	
	600	Inlet	Nil	0.8	8.0	10.0	3.0	68.4	9.8	87.4
		Outlet	4.0	Nil	Nil	24.6	65.6	2.6	3.2	
	800	Inlet	Nil	0.6	8.2	9.6	3.2	68.2	10.2	82.9
		Outlet	5.6	Nil	Nil	22.0	65.0	3.8	3.6	
	1000	Inlet	Nil	0.6	8.2	9.6	3.2	68.2	10.2	79.9
		Outlet	6.0	Nil	Nil	21.0	64.0	4.6	3.4	

TABLE 3—Activity Results of Steam-Oxygen-Methane Reactions

[Perheater Temp. 600°C, Reactor Temp. 850°C, Steam/Gas Ratio 0.5, Oxygen/Gas Ratio 0.5]

Catalyst	Space velocity		Gas Composition, % by volume							Conversion of CH_4, %
			CO_2	O_2	CnHm	CO	H_2	CH_4	N_2	
A	400	Inlet	Nil	1.0	7.6	10.4	2.8	68.4	9.8	97.8
		Outlet	7.2	Nil	Nil	32.0	56.2	0.6	4.0	
	600	Inlet	Nil	1.0	7.6	10.4	2.8	68.4	9.8	97.0
		Outlet	8.0	Nil	Nil	30.4	56.6	0.8	4.2	
	800	Inlet	Nil	0.8	7.4	9.6	2.8	69.2	10.2	95.6
		Outlet	8.2	Nil	Nil	30.0	56.4	1.2	4.2	
	1000	Inlet	Nil	0.8	7.4	9.6	2.8	69.2	10.2	94.2
		Outlet	9.4	Nil	Nil	29.2	56.0	1.6	3.8	
B	400	Inlet	Nil	0.8	7.8	11.0	4.4	67.0	9.8	94.8
		Outlet	7.2	Nil	Nil	29.0	58.6	1.4	3.8	
	600	Inlet	Nil	0.8	7.8	11.0	4.4	67.0	9.0	93.4
		Outlet	7.6	Nil	Nil	28.4	58.0	1.8	4.2	
	800	Inlet	Nil	0.8	7.6	9.6	4.0	68.8	9.2	90.0
		Outlet	10.8	Nil	Nil	27.2	54.6	3.0	4.4	
	1000	Inlet	Nil	0.8	7.6	9.6	4.0	68.8	9.2	87.9
		Outlet	13.4	Nil	Nil	26.6	57.6	3.8	4.6	
C	400	Inlet	Nil	0.8	6.4	12.0	3.4	66.6	10.8	95.9
		Outlet	6.2	Nil	Nil	31.8	57.4	1.0	3.6	
	600	Inlet	Nil	0.8	6.4	12.0	3.4	66.6	10.8	95.2
		Outlet	6.4	Nil	Nil	31.4	57.4	1.2	3.4	
	800	Inlet	Nil	0.8	8.0	10.0	3.0	69.2	9.0	94.6
		Outlet	6.8	Nil	Nil	30.8	57.6	1.4	3.4	
	1000	Inlet	Nil	0.8	8.0	10.0	3.0	69.2	9.0	93.1
		Outlet	10.0	Nil	Nil	28.0	56.4	1.8	3.8	
D	400	Inlet	Nil	1.0	7.8	11.2	3.4	66.2	10.4	94.0
		Outlet	9.6	Nil	Nil	29.6	55.0	1.6	4.2	
	600	Inlet	Nil	1.0	7.6	10.8	3.4	66.6	10.6	91.4
		Outlet	8.2	Nil	Nil	28.2	57.0	2.2	4.4	
	800	Inlet	Nil	0.8	8.4	11.0	3.2	66.4	10.2	89.8
		Outlet	10.4	Nil	Nil	26.4	56.2	2.6	4.4	
	1000	Inlet	Nil	0.8	8.4	11.0	3.2	66.4	10.2	87.6
		Outlet	11.4	Nil	Nil	26.0	55.0	3.4	4.2	
E	400	Inlet	Nil	0.8	7.6	8.8	3.2	70.2	9.4	93.6
		Outlet	6.4	Nil	Nil	31.2	56.8	1.8	3.8	
	600	Inlet	Nil	0.8	7.6	8.8	3.2	70.2	9.4	91.0
		Outlet	8.2	Nil	Nil	29.4	55.8	2.6	4.0	
	800	Inlet	Nil	0.6	7.8	8.6	3.0	69.2	10.8	87.6
		Outlet	8.8	Nil	Nil	28.2	56.0	3.2	4.6	
	1000	Inlet	Nil	0.6	7.8	8.6	3.0	69.2	10.8	85.5
		Outlet	8.2	Nil	Nil	28.0	55.2	3.8	4.8	



NiO, % by weight

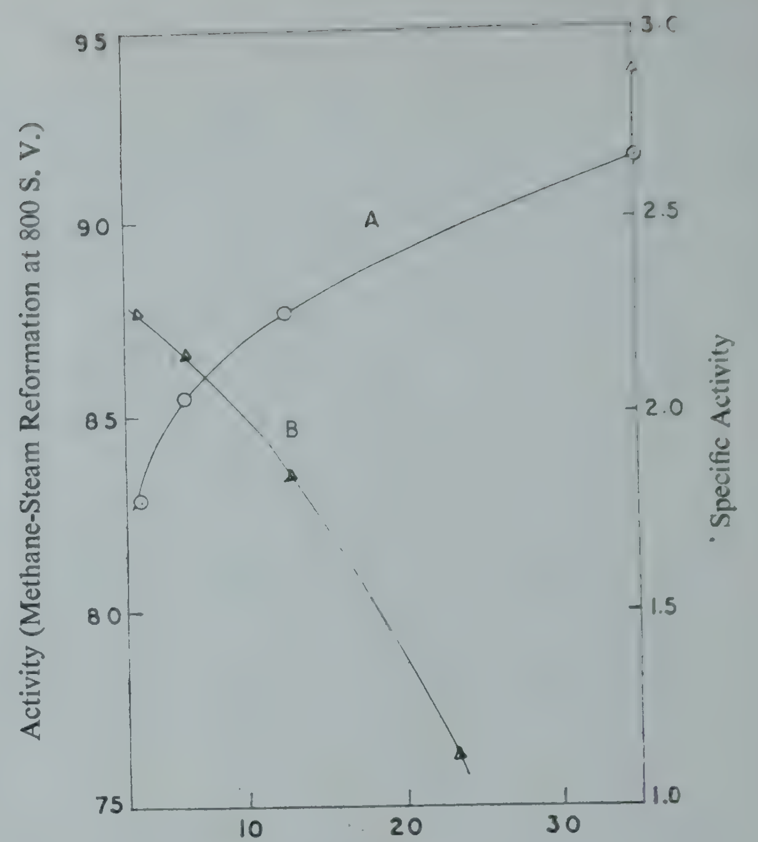
Fig. 1—Dependence of Specific Surface on Nickel Content

Specific activity has been defined as activity per metre square of the specific surface.

It is observed from Curve A of Fig. 2 that in general activity increases with nickel content of the catalyst. Only exception is catalyst B which shows less activity than catalyst C in spite of having higher nickel content. It is interesting to note that the effect of nickel content on activity is much more prominent in case of catalysts C, D and E having comparatively lower nickel concentrations compared to what is observed in case of catalyst A. It may be quite possible that increase in nickel concentration upto certain extent probably in the region of 10 per cent, is accompanied by almost proportionate increase in activity under the experimental conditions of the present investigation and further increase in nickel content beyond this concentration increases the activity of the catalyst only marginally.

It is observed from curve B of Fig. 2 that in genera specific activity of the catalysts decreases with increase in nickel content. Catalysts B, C, D and E having nickel content in decreasing order possess specific activity in reverse order. This decrease in activity per unit surface with increasing nickel content may have relation with distribution of nickel on surface which probably changes with concentration. But only exception to this is observed in case of catalyst A which possesses maximum specific activity though its nickel content is highest. This again shows that method of preparation may have a definite bearing on the activity of the catalyst.

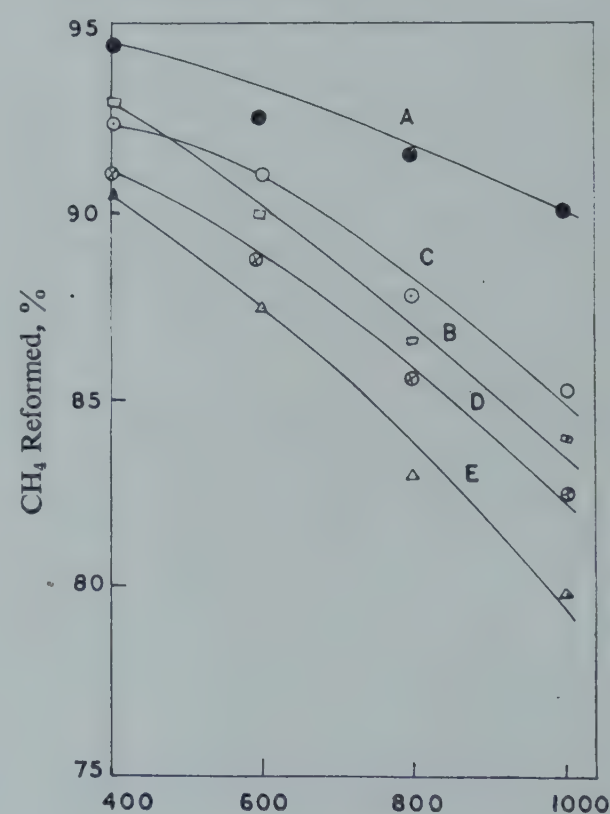
The curves of Fig. 3 show the variation in conversion efficiency of the catalysts with space velocity. On comparing the conversion efficiency with changing space



NiO, % by weight

Fig. 2—Effect of Nickel on Activity (A) and Specific Activity (B)

velocity it is observed that the decrease in conversion efficiency at higher space velocity is less with the catalyst having higher nickel content. Thus with catalyst A having highest nickel content the fall in conversion with



Space Velocity

Fig. 3—Effect of Space Velocity on Steam Reformation

increasing space velocity is least. On the other hand catalyst E having least nickel shows maximum fall with increase of space velocity. It is therefore apparent that the catalyst having higher nickel will be of more advantage over the one having less nickel at higher space velocities. However, catalyst B is an exception and does not follow similar trend. The decline in conversion efficiency of this catalyst with increase of space velocity is rather unexpected and more rapid than what is observed in case of catalysts C and D both of which have much less nickel than that of catalyst B.

Activity in Presence of Steam and Oxygen: The results of activity tests carried out in presence of steam and oxygen have been presented in Table 3. Variation of conversion efficiency with space velocity for all the catalysts tested have been shown by the curves in Fig. 4. It is observed from Table 3 and the curves in Fig. 4 that the conversion efficiencies of the different catalysts, in presence of both steam and oxygen maintain the same relative positions as in the case of reaction with steam alone. However efficiencies of all the catalysts are relatively higher in presence of oxygen. This may be due to the fact that the mechanism of heat transfer to the reaction sites is definitely more efficient when partial combustion with oxygen takes place in the catalyst bed itself.

Reactions in presence of steam and oxygen also show that catalyst having higher nickel content is more active.

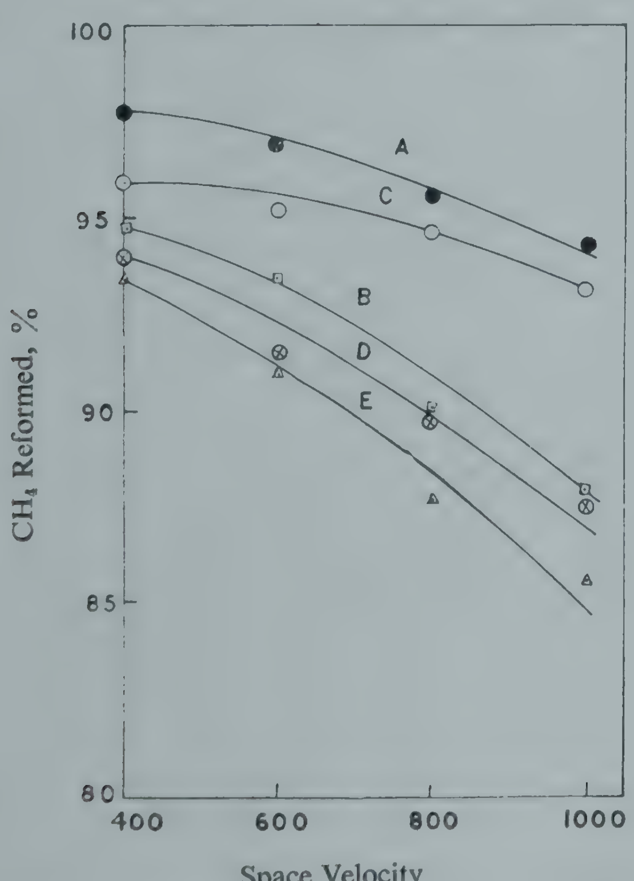


Fig. 4—Effect of Space Velocity on Steam Oxygen Reformation

Catalyst B is an exception which in spite of its higher nickel content shows less activity and more decline in conversion at higher space velocities than what is observed with catalyst C. Decrease in conversion efficiency with increasing space velocity is relatively less with catalyst having higher nickel content so far as catalysts C, D and E are concerned. Catalyst A having highest nickel content is most active but decrease in conversion with increase of space velocity is more than what is observed in case of catalyst C having lower nickel content.

Comparative Assessment: From all the observations made in the foregoing discussions it appears that nickel concentration of the catalyst determines its activity to a great extent. However, the exceptions observed in case of catalysts A and B appear to be due to the fact that apart from nickel content other factors like mode of preparation of the carrier and incorporation of the active components and composition and structure of the finished catalyst also contribute to the activity.

The results of the present investigation show that performance of none of the catalysts studied appears to be specific either for steam reformation or for reformation in presence of steam and oxygen under the conditions of experiments. Relative efficiencies of the catalysts are more or less similar in both type of reactions. However, it appears that catalyst A is most efficient for steam methane reformation. The efficiencies of both catalysts A and C are more or less similar, but superior to the other catalysts studied, for reformation in presence of steam and oxygen specially at higher space velocities.

However, in prolonged operations at lower temperature and higher pressures the efficiency of all the catalysts may not be identically affected and in such case the catalysts may exhibit their specificity for particular service conditions. Further studies are being continued.

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A quick and accurate method has been developed for the estimation of water-soluble phosphate in single and triple superphosphates. The procedure consists in titrating a dilute aqueous extract of the superphosphate sample against 0.1 N caustic soda by the high frequency or conductometric method. From the breaks in the curve, the amounts of free phosphoric acid and monocalcium phosphate in the sample are estimated.

Estimation of Water-Soluble P_2O_5 in Normal and Triple Superphosphates Using High Frequency Titrimetry and Conductometry

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In the manufacture of superphosphates, estimation of water-soluble P_2O_5 in the product is of considerable importance. The standard volumetric and gravimetric methods are time-consuming. Hence, for plant control purposes, methods for quick estmation of water-soluble P_2O_5 in superphosphates would be welcome. Guthric and Nace[1] have described a titrimetric method for estimation of free acid and monocalcium phosphate in superphosphate. Since free sulphuric acid is not normally present in superphosphates the free acid would be phosphoric acid and this together with monocalcium phosphate would comprise the water-soluble phosphate in the material.

According to them[1], the sample of superphosphate is extracted with water and the solution is titrated with a standard solution of sodium hydroxide in two stages with appropriate indicators. The first stage gives the free acid and the second an approximate result for the primary calcium phosphate. As superphosphate samples contain fluoride and fluosilicate ions, the indicators are not always stable and accurate results cannot be easily found by using indicators. An electrometric method

would give a better result than that obtained by using indicators. In this context, the application of high frequency titrimetry seemed promising as many workers[2] have applied this technique in the estimation of acids and bases in aqueous and non-aqueous media. In several communications[3-6] from this laboratory also, high frequency titrimetry has been used in developing analytical methods in the field of fertilizer technology. In the case of superphosphates, high frequency titrimetry has already been applied for the determination of free acidity[5].

In the present paper a method has been developed for rapid and accurate determination of water-soluble phosphate present in superphosphate samples using high frequency titrimetry and conductometry. The water-soluble components, viz. monocalcium phosphate (primary calcium phosphate) and phosphoric acid which contribute towards the water-soluble phosphate content in superphosphates are titrated in pure forms singly as well as in combinations. The use of conductometry is not always advocated as the electrodes may be spoiled because of the presence of corrosive substances present in superphosphates; this corrosion is not possible in high frequency titrimetry as the electrodes are not in direct contact with the solution to be titrated. However, commercial samples of the superphosphate solutions are titrated by using both high frequency titrimetry and conductometry.

Experimental

All the chemicals used in these investigations were of A. R. or G. R. grade unless otherwise stated. All the solutions were made in deionized, carbon dioxide-free water.

The conductometric titrations are carried out at $35 \pm 1°C$ with an Hungarian-make conductometer* having a bell type electrode with three platinum rings.

The high frequency titrimeter used in these investigations is also of Hungarian make.† It is designed to operate at 140 Mc/s frequency and used for the measurement of high frequency conductivity where there is no galvanic connection between the measuring system formed by the electrodes and the solution to be tested.

The cell used in the instrument is of capacitive type and the solution to be titrated in it is stirred with a special type of vibrating magnetic stirrer. The electrodes are connected through a capacitor to the oscillating circuit. The solution to be titrated is taken in a pyrex glass beaker of 250 ml. capacity and is placed between the two metallic rings forming the two electrodes of the cell. All the titrations are done in very dilute solutions and the total dilution in each case remains the same and the final volume is such that its level is slightly higher than the upper edge of the upper electrode. In all the titrations mentioned, the optimum concentration of the salt mixtures and commercial samples that should be taken in the titration cell for the maximum sensitivity of the instrument to get sharp breaks in the titration curves are first found out by trial and error.

The commercial superphosphate samples generally available are aged ones and they do not contain free acid in an appreciable amount, in aged superphosphate samples only monocalcium phosphate is the source of water-soluble phosphate. All the samples which are titrated are aged ones and do not contain free phosphoric acid except in two cases where free acidity is also present. Other constituents of superphosphate are calcium sulphate, fluoride, ferric oxide, aluminium oxide and other minor constituents, which do not affect the titration curves in the dilute solution in which the titrations are carried out. The following titrations were carried out: (a) pure monocalcium phosphate monohydrate (primary calcium phosphate), (b) pure monocalcium phosphate monohydrate along with free phosphoric acid, (c) commercial samples of fresh and aged normal and triple superphosphates.

For comparison of the results obtained by present method with those by the standard methods, the free acid in the samples is determined by extraction with acetone and ether (1:1) and the acid extracted is titrated with standard caustic soda solution in presence of methyl yellow indicator[7], which is more stable and gives sharper end points. The P_2O_5 due to free acid is substracted from the total water-soluble P_2O_5 obtained by AOAC[8] method to give P_2O_5 due to monocalcium phosphate in the samples.

Results and Discussion

The three common phosphates of calcium are of great importance because of their use as fertilizer, their presence in soils and their use in numerous commercial products. Comprehensive data are available on their preparation, properties and composition. According to Larson[9], monocalcium phosphate is completely soluble in pure water when dissolved upto a concentration of 10 g./l. at 25°C and all of salt dissolved can be accounted for by determining the P_2O_5 present in the solution,

* Radelkisz type OK-102.

† developed by Prof. E. Pungor and manufactured by Radelkisz, Budapest. It is known as oscillotitrator type OK-302.

above this concentration some hydrolysis takes place. In all the titrations carried out in the present investigation the concentration of monocalcium phosphate (primary calcium phosphate) does not exceed the above limit; in fact very dilute solutions are taken. In case of pure monocalcium phosphate, the concentration varies from 2.4 to 2.8 g./l, whereas in commercial samples it varies from 4.5 to 7 g./l. depending upon the water-soluble P_2O_5 contents. It is observed that when dilute solutions, mentioned above, are taken as stock solution, no hydrolysis is encountered and accurate results are obtained.

The results of high frequency titrimetric determinations of different dilute solutions of pure monocalcium phosphate are given in Table 1 and a typical titration curve is given in Fig. 1, curve 1. The curve has two breaks —the first at about half of the volume of the titrant added to that corresponding to second break. As the titration proceeds, there is no turbidity or precipitate formation upto the first break, but after this when more alkali is added turbidity appears and a white precipitate is formed at the second break. The precipitate after filtering and washing is analysed for calcium and phosphate ions. It is found that the CaO : P_2O_5 ratio varies from 1.25 to 1.5 by weight depending upon the time of addition of titrant, concentration of the solution titrated, etc. The ratio of CaO to P_2O_5 found does not correspond exactly to dicalcium phosphate.

Monocalcium phosphate (mono-basic calcium phosphate) is an acid salt and hence it reacts with sodium hydroxide giving breaks in the titration curve. $H_2PO_4^-$ ion is first neutralized with the formation of dicalcium phosphate.

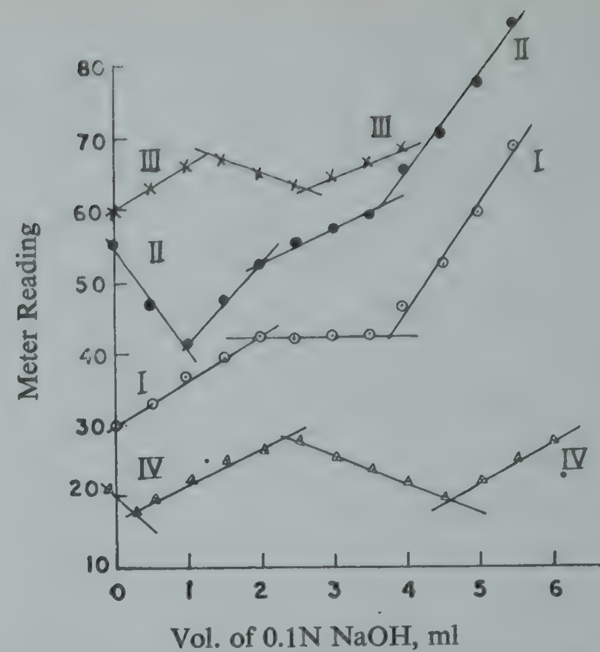

Fig. 1—High Frequency Titration of Monocalcium Phosphate Solution Against 0.1 N Caustic Soda

I—10 ml. Ca $(H_2PO_4)_2$ Stock Solution
II— 5 ml. $Ca(H_2PO_4)_2$+3cc., 0.1N H_3PO_4
III—10 ml. Superphosphate Stock Solution
IV—20 ml. Fresh Superphosphate Solution Containing Free H_3PO_4

$$Ca(H_2PO_4)_2+2NaOH=CaHPO_4+Na_2HPO_4+2H_2O$$

This neutralization proceeds upto first break in the titration curve; upto this point no precipitate is formed as the amount of dicalcium phosphate formed is soluble in the volume of the remaining solution present in the

TABLE 1—High Frequency Titration of Monocalcium Phosphate against Standard Caustic Soda Solution

Stock Solution: A = 0.6426 g./250 ml.
B = 0.6154 „
C = 0.6230 „

No. of Stock Solution	Vol. of Stock Solution for Titration, cc.	pH of the Solution Titrated	Monocalcium Phosphate Monohydrate, g.			Error, %	
			By Std. Method	By High Frequency	By Conductometry	High Frequency	Conductivity
A	5.0	4.75	12.484	12.730	12.850	1.983	2.951
	10.0	4.45	25.012	25.510	—	1.992	
B	5.0	5.30	11.884	11.615	12.185	2.280	2.550
	10.0	5.25	23.867	24.224	—	1.500	—
C	5.0	4.95	11.961	12.152	11.750	1.605	1.773
	10.0	4.70	23.721	23.480	—	1.029	—

titration cell. When more alkali is added, turbidity appears at once which indicates the formation of an insoluble salt, presumably tricalcium phosphate mixed with calcium hydroxide or other complex basic phosphates. The pH of the solution at the first break is between 5.5 to 6.5 and at the second break which is nonstoichiometric it is above 9.2; this also shows the formation of basic phosphates. The values of water-soluble P_2O_5 in the solutions titrated are calculated from the first break in the titration curve according to the above equation. The error in high frequency titrimetric determination of pure monocalcium phosphate solutions alone does not exceed 2 per cent (Table 1).

When a mixture of solutions of pure monocalcium phosphate and pure phosphoric acid is titrated by the high frequency method both the constituents of the mixture can be easily estimated. In curve II of Fig. 1, which is one of such titration curves, the first break shows the one-third neutralizations point of phosphoric acid; the second break is due to the conversion of monocalcium phosphate to dicalcium phosphate[10] and the last break corresponds to the complete neutralization of phosphoric acid and monocalcium phosphate. It is seen from the results (Table 2) that the error in the estimations when computed with the standard methods does not exceed 3 per cent.

When dilute solutions of pure monocalcium phosphate are titrated according to the ordinary conductometric method, results similar to those obtained by high frequency titrimetry are obtained; the nature of titration curves is also same (Fig. 2). But here concentration of the pure salts taken for titration should not exceed 12.85 mg./225 ml. as stronger solutions do not give accurate results. In presence of phosphoric acid, the

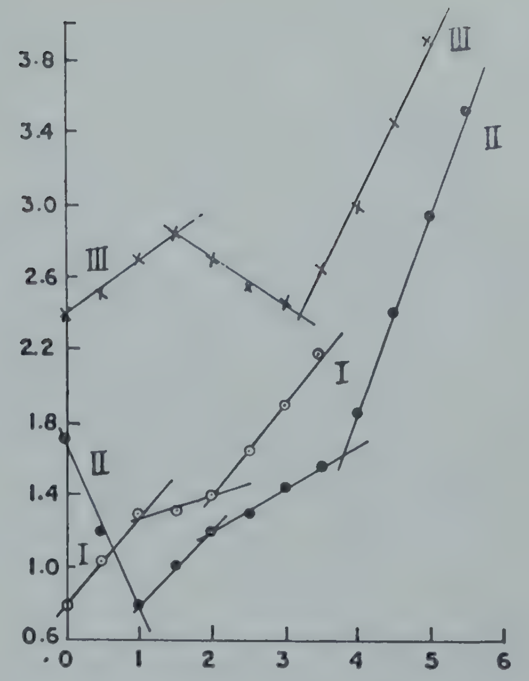

Fig. 2—Conductometric Titration of Superphosphate Solution Against Standard Caustic Soda

I— 5 ml. of Monocalcium Phosphate Stock Solution
II— 3 ml. 0.1N H_3PO_4+5 cc. Monocalcium Phosphate Stock Solution
III—10 ml. Superhposphate Stock Solution

first break in the titration curve is due to one-third neutralization of free phosphoric acid, the second break corresponds to the conversion of monocalcium phosphate present to dicalcium phosphate[10] and the third break is due to neutralization of remaining acidic constituents in the solution. In the titration of the pure (Tables 1 & 2) salt, the error is 4 per cent which is more in comparison with high frequency titrations.

In Table 3 and Figs. 1 & 2 are given the results of high frequency as well as conductometric titrations of different commercial samples of normal and triple super-

TABLE 2—High Frequency Titration of Monocalcium Phosphate in Presence of Standard Phosphoric Acid against Standard Caustic Soda Solution

No.	Phosphoric Acid, mg.					Monocalcium Phosphate Monohydrate, mg.				
	Taken	By High Frequency	By Conductometry	Error, %		By. Std. Method	By High Frequency	By Conductometry	Error, %	
				High Frequency	Conductometry				High Frequency	Conductometry
1.	9.798	9.625	10.094	1.71	3.02	12.484	12.745	12.780	2.104	2.387
2.	9.798	9.705	—	0·98	—	17.820	18.022	—	1.162	—
3.	9.798	9.985	—	1.90	—	23.720	23.480	—	1.025	—

TABLE 3—HIGH FREQUENCY TITRATION OF SUPERPHOSPHATE SOLUTION AGAINST STANDARD CAUSTIC SODA

Sample No.	P_2O_5, %					
	By Std. Method	By High Frequency	Error, %	By Conductometry	Error, %	pH
1.	17.350	17.853	2.907	18.000	3.823	4.250
2.	16.924	17.251	1.934	—	—	4.000
3.	15.882	16.124	1.531	—	—	—
4.	17.509	17.000	2.805	18.550	2.412	4.350
5.	18.052	17.754	1.627	—	—	4.400
6.	16.075	16.425	2.187	—	—	—
*7.	16.854	17.092	1.416	17.480	3.726	4.150
8.	19.017	19.435	2.200	20.708	3.636	3.900
9.	18.600	18.738	0.831	19.073	2.543	—
10	37.376	36.350	2.000	38.650	3.417	4.950
11.	38.144	38.782	1.674	—	—	4.250
*12.	48.215	49.401	2.460	—	—	—

*Sample nos. 7 and 12 contain 4.5 and 9.8 per cent free phosphoric acid respectively.

phosphate. For the estimations,** a stock solution of each sample is prepared by extracting 1.5 to 2 g. of the sample with distilled water and the volume is made upto 250 ml. Five to 10 ml. of these stock solutions are titrated for water-soluble P_2O_5 against standard 0.1 N caustic soda. In these titrations with commercial superphosphates, sharp breaks are obtained even by ordinary conductometry. If the superphosphate does not contain any free acid, it gives only two sharp breaks one of which occurs at about half the volume of titrant corresponding to the other; in case of samples which contain some free acidity, the first break corresponds to one-third neutralization of the acid. Fig. 1 (curve III) corresponds to the high frequency titration of a sample which does not contain any free acid and has only two breaks, whereas the curve IV corresponds to the high frequency titration of a fresh sample of superphosphate containing free phosphoric acid. The one-third neutralization of free acid is shown by the first break in this curve, the second break is due to the conversion of monocalcium phosphate present in the solution to dicalcium phosphate and the third is due to the complete neutralization of remaining acidic constituents. The conductometric titration curve (Fig. 2, curve III) of a commercial sample which does not contain any free acid has only two sharp breaks one of which occurs at about half the volume of titrant corresponding to the other. The results of estimation (Table 3) when compared with those obtained by the standard methods indicate an error below 4 per cent.

** According to AOAC method[8] for determination of water-soluble phosphate.

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Polarographic behaviour of Cr^{6+} and Fe^{3+} has been studied in 0.2M potassium chloride + 0.3M triethanolamine +0.01% gelatin as base electrolyte at different pH values. Well separated waves of Cr^{6+} and Fe^{3+} with $E_{\frac{1}{2}}$, −0.176 and −0.48 volts respectively, obtained at pH 8.0, have been utilized in the estimation of iron and chromium in stainless steel without prior separation of either of the two. The percentage recovery has been found to be 98 to 101 per cent for both. The errors in estimation have been found to be ± 1.5 per cent when compared with standard methods.

Simultaneous Estimation of Iron and Chromium in Stainless Steel by Polarographic Method

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In chemical industry, stainless steel is widely used for the fabrication of various equipment. For checking the quality of this material, it is frequently necessary to analyse it for its important constituents. The present work was undertaken to develop a polarographic method of simultaneous estimation of iron and chromium in stainless steel.

Polarographically chromium in steel has been estimated by using the step given by chromate in a sodium or potassium hydroxide base electrolyte[1]. The alkali hydroxide precipitates iron completely from the solution and chromium is appreciably coprecipitated with the iron hydroxide. It is, however, claimed that the effect of this coprecipitation loss is greatly reduced by using the standard addition method.[2]. The same step of chromate has also been used for the determination of chromium in cement[2], glass[4] and ruby[5,6]. In the present investigation a polarographic study was carried out of Cr^{6+} and Fe^{3+} in potassium chloride and triethanolamine supporting electrolyte at different pH values and a method has been evolved for simultaneous determination of chromium and iron in stainless steel without prior separation, thus avoiding the possible loss due to the coprecipitation of chromium with iron.

Experimental

Polarograms were recorded on a LP-60 self-recording polarograph. A fine capillary with the characteristics $m^{2/3}\ t^{1/6} = 2.57$ was used throughout the work. All studies were carried out in a H type Novak cell of 20 ml. capacity[7]. The second arm of the cell was isolated by a sintered disc and agar bridge. The circuit consisted of a saturated calomel electrode (S.C.E.) as reference, agar bridge and a dropping mercury electrode. Nitrogen was bubbled through the cell for 15 min. to effect deaeration before each experiment. Analytical grade mercury was used in the dropping electrode. All studies were carried out at 30°C. All chemicals were of Analar quality. Adco electronic pH meter with glass and calomel electrode was used to measure the pH of the experimental solutions.

Stock solutions of chromate were prepared by dissolving potassium chromate in water and the solutions were standardized against sodium thiosulphate iodometrically[8]. Stock solutions of Fe^{3+} were prepared by dissolving iron metal in hydrochloric acid and standardized volumetrically[9]. A mixture of 0.3M triethanolamine and 0.2M potassium chloride was used as supporting electrolyte; 0.01 to 0.02% solution of gelatine was used as maxima suppressor.

Standard stainless steel samples of AISI type 347, 321, 316 and 304 have been used for the standardization of the method.

The chromium and iron contents of steel samples have been determined by using standard methods[8,9]. Polarographic behaviour of Cr^{6+} and Fe^{3+} was studied separately and in mixtures at different pH in a base electrolyte consisting of 0.2M potassium chloride and

TABLE 1—Effect of pH on the Polarographic Behaviour of Cr^{6+}, Fe^{3+} and Their Mixtures

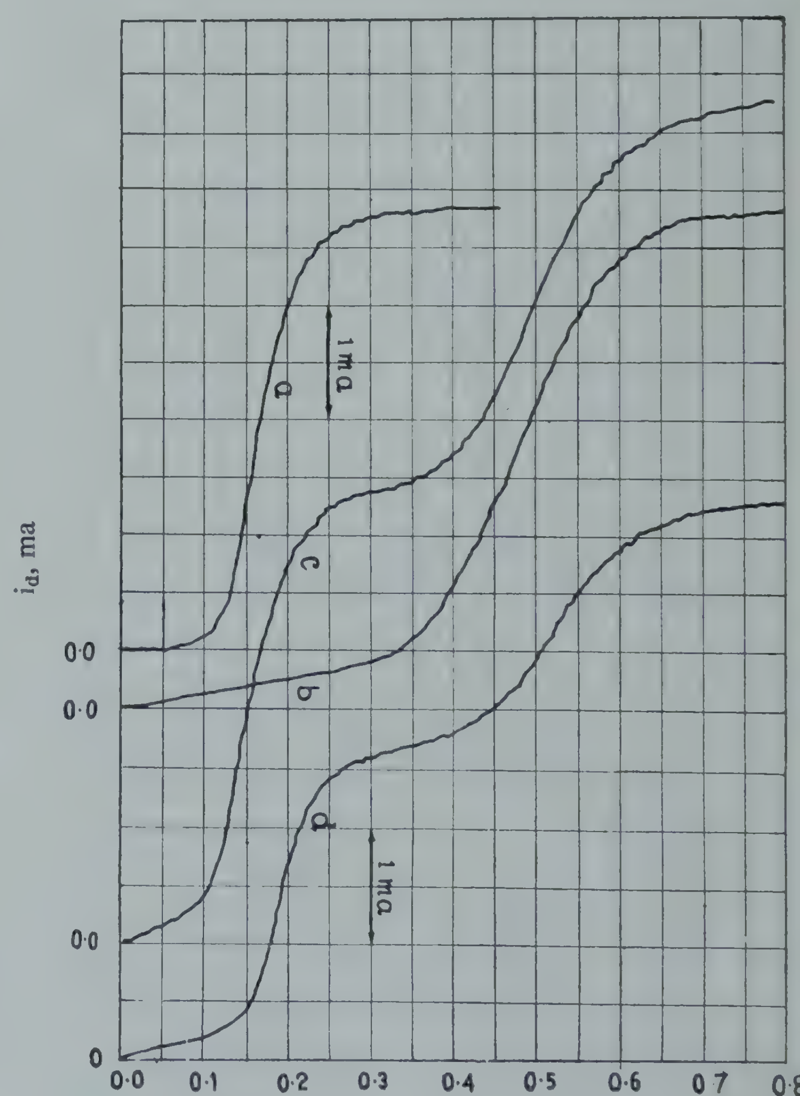
[Base electrolyte — 0.2M KCl + 0.3M Triethanolamine + 0.02% gelatin]

pH	Cr^{6+} Alone		Fe^{3+} (2.0mM) Alone		Mixture of Fe^{3+} (2.00) Cr^{6+} (0.4mM)+	
	Nature and $E_{\frac{1}{2}}$, volts	i_d, mA	Nature & $E_{\frac{1}{2}}$ volt	i_d, mA	Nature and $E_{\frac{1}{2}}$, volt	i_d, mA
7	Wave starts form zero applied potential		−0.40 (well-defined)	2.89	1. Wave starts from zero applied 2. −1.03	 1.40
8	0.16 (Well-defined)	4.80	−0.51 (well-defined)	6.150	1. − 0.16 (Cr^{6+}) 2. − 0.575 (Fe^{3+})	5.62 3.72
9	0.28 (welldefined)	5.0	−0.65 (well-defined)	7.98	1. − 0.34 (Cr^{6+}) 2. − 0.57 (Fe^{3+}) 3. − 0.775 (not clear)	2.80 3.70 2.40
10	(i) Wave starts from zero-potential (ii) −0.445	11.02 ma	−0.80 (well-defined)	7.05	1. Wave starts from zero applied potential 2. Overlapping 3. −0.740 (not clear)	 5.80

0.3M triethanolamine with gelatin as maximum suppressor. The pH of the solutions was adjusted with dilute hydrochloric acid and sodium hydroxide solutions. Polarograms were recorded and the results are given in Table 1 and Fig. 1.

Calibration of Working Graph: To a supporting electrolyte containing 0.2M potassium chloride, 0.3M triethanolamine and 0.01 per cent gelatin, various amounts of Fe^{3+} and Cr^{6+} solutions were added. The pH of the solutions was adjusted to 8.0 by a pH meter. The solutions were then made upto the mark and a series of polarorgams were recorded. Diffusion currents were calculated and plotted against concentration of Cr^{6+} and Fe^{3+} (Fig. 2).

Procedure for the Treatment of Stainless Steel for Polarographic Analysis: Stainless steel sample was washed with hot toluene to remove any oily material. About 50 mg. of the cleaned sample was taken in a beaker and dissolved in 8 ml. of sulphuric acid (1:6) by slowly heating. To the clear solution, 1 ml. of 1 per cent silver nitrate solution and 0.9 g. of solid ammonium persulphate was added and boiled to get a permanent pink coloration. The excess persulphate was then decomposed by boiling for 5 min. The solution was then again boiled with 3 ml. of 3 N hydrochloric acid to decompose permanganate. The resulting solution was then cooled and diluted to 100 ml. in a volumetric flask. 100 ml. of the solution was taken in a beaker, to which 10 ml. of 2M potassium chloride, 10 ml. of 3M trietha-



Ede vs SCE, volt

Fig. 1

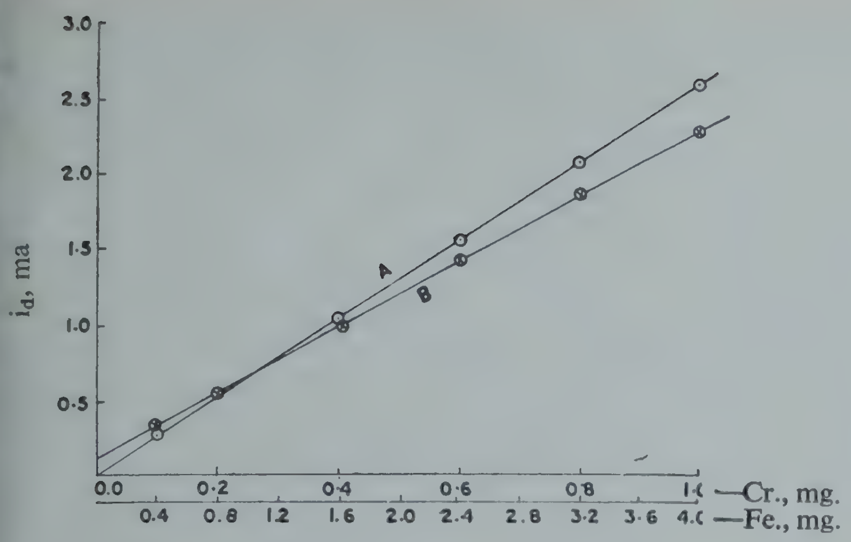


Fig. 2—Calibration Curve

A—Cr, B—Fe

nolamine and 1 ml. of 1 per cent gelatin was added and the pH of the solution was adjusted to 8.0 after dilution. The solution was then made upto 100 ml. to get 0.2M potassium chloride, 0.3M triethanolamine and 0.01 per cent gelatin. A portion of this solution was transferred to polarographic cell and the polarogram was recorded. The diffusion currents were calculated and the percentage of iron and chromium in steel was calculated. The results of analyses of various known mixtures of Cr^{6+} and Fe^{3+} and stainless steel samples are given in the Tables 3 and 4.

Results and Discussion

In an attempt for simultaneous estimation of chromium and iron in steel by a polarographic method, a mixture of potassium chloride and triethanolamine, after careful adjustment of the pH, has been used in the present study as base electrolyte. Triethanolamine with Fe^{3+} forms a complex for which a reduction step at $E_{\frac{1}{2}}$ −1.01 volt is reported in a highly alkaline media[10,11]. With the use of the base electrolyte referred to above, well separated waves of Cr^{6+} and Fe^{3+} have been obtained and utilized for the determination of iron and chromium in steel.

As a first step, the effect of pH on the polarographic behaviour of Cr^{6+} and Fe^{3+}, separately and in mixtures, in the potassium chloride triethanolamine base electrolyte, has been studied, Chromate gives well defined steps at pH 8.0 and 9.0 with $E_{\frac{1}{2}} = -0.16$ and -0.28 volts respectively, while the wave at pH 7.0 starts from zero applied potential. At pH 10.0 a wave with $E_{\frac{1}{2}} = -0.445$ volts with low diffusion current is observed. Half wave potentials of Cr^{6+} are found to shift to more negative value as the pH changes from 7.0 to 10.0; this may be due to the complexing of Cr^{6+} with triethanolamine. Fe^{3+} also gives well defined waves with varying half wave potential depending on the pH of the basal solution, this also indicates the complexing of Fe^{3+} with triethanolamine. The best separation of Cr^{6+} and Fe^{3+} waves with a difference of 0.35 and 0.37 volt in the half wave potential is observed at pH 8.0 and 9.0 respectively when they are present in a mixture. At other pH values the waves are either distorted or superimposed. Because of higher diffusion currents of Cr^{6+} and Fe^{3+} at pH 8.0, this pH value is preferred to pH 9.0 for the polarographic analysis of the mixture.

The details of the polarographic behaviour of Cr^{6+} and Fe^{3+} separately and in mixtures have been worked out (Table 2, Fig. 1). Well defined polarographic waves of Cr^{6+} and Fe^{3+} are obtained at pH. 8.0 in 0.2 M potassium chloride and 0.3M triethanolamine with 0.01 per

TABLE 2—VALUE OF SLOPE, $E_{\frac{1}{2}}$, I_d AND I OF Cr^{6+}, Fe^{3+} AND THEIR MIXTURES

(Base electrolyte −0.2M KCl + 0.3M Triethanolamine + 0.01% gelatin; pH 9.0

Experimental Solution,	$E_{\frac{1}{2}}$ SCE Volt	i_d, mA	Slope	$1 = \frac{i_d}{cm^{2/3}t^{1/6}}$	Value of n from Ilkovic Equation	Nature
1. 0.25mM Cr^{6+}	−0.176	3.46	0.04730	5.389	3.00	Irreversible
2. 1.0mM Fe^{3+}	−0.483	3.43	0.109	1.339	—	Irreversible
Mixture of		3.45	0.0476	5.375	3.00	Irreversible
3. 0.25mM Cr^{6+} and	−0.168	2.95	0.109	1.148	—	Irreversible
1.0mM Fe^{3+}	−0.505					
AISI Type 316	−0.192	2.95	—	—	—	—
Stainless Steel						
(5.17mg.)	−0.0535	2.00	—	—	—	—

cent gelatin as maximum suppressor (Fig. 1, A & B) and are found to be diffusion-controlled. The slope for the plot of log $i/(i_{d}-i)$ against E_{de} for chromate is found to be 0.047 and $E_{\frac{1}{2}}$ is found to change with the concentration of Cr^{6+} (Table; 3) this confirms the irreversible behaviour of chromate wave. The value of n has been calculated from Ilkovie equation. The diffusion coefficient D has been obtained by conductivity of chromate solution at infinite dilution which has been given as $1.07 \times 10^{-5}/cm^2/sec.^{-1}$ by Kolthoff and Lingane[12]. By substituting the appropriate values of i_d, C.D and $m^{2/3}$ $t^{1/6}$ to Ilkovic equation, the value of n has been calculated and found to be 3, which confirms the three electron reduction of Cr^{6+} according to equation $Cr^{6+} + 3e\ Cr^{3+}$.

The values of $E_{\frac{1}{2}}$ vs SCE and I for chromate (0.25mM) are calculated to be-0.176 volt and 5.39 The plot of log $i/(i_{d}-i)$ against $^{-}E_{de}$ for Fe^{3+} is found to be a straight line with a slope of 0.109, showing the system to be irreversible. The values of $E_{\frac{1}{2}}$ and I are found to be −0.483 volt and −1.34 respectively. Typical polarograms of mixtures of Cr^{6+} and Fe^{3+} as well as of solutions of stainless steel samples (316 Type AISI) are given in Fig. 1D). Well separated waves of chromium and iron in stainless steel solutions, similar to those of pure mixtures of Cr^{6+} and Fe^{3+}, are obtained which confirm that the waves are free from interferences due to manganese, molybdenum, carbon and silicon, etc., present in steel.

For finding the suitability of the polarographic method for the estimation of Cr^{6+} and Fe^{3+} in stainless steel, the diffusion currents of Cr^{6+} and Fe^{3+} are plotted against concentration. The plots are found to be linear (Fig. 2), and are used as standards for the estimation of chromium and iron in stainless steel samples. To check the present method, various known mixtures of Cr^{6+} and Fe^{3+} have been analysed (Table 3). The percentage

TABLE 3—DETERMINATION OF Cr^{6+} AND Fe^{3+} IN KNOWN MIXTURES

[*Base electrolyte*: 0.2MKC1 + 0.3M Triethanolamine + 0.01% gelatin; pH. 8.0]

Sl. No.	Cr^{6+} Taken, mg.	i_d, mA.	Cr^{6+} found Polarographically, mg.	% Recovery	Fe^{3+} Taken, mg.	i_d, mA	Fe^{+} Found Polarographically, mg.	% Recovery
1.	0.15	0.370	0.15	100.00	1.10	0.701	1.11	100.9
2.	0.30	0.755	0.298	99.33	1.50	0.920	1.50	100.0
3.	0.40	1.065	0.402	100.5	1.80	1.083	1.798	99.88
4.	0.50	1.260	0.493	98.5	2.00	1.205	2.013	100.65
5.	0.60	1.538	0.599	99.83	2.50	1.495	2.520	100.08
6.	0.70	1.799	0.699	99.86	3.00	1.755	2.975	99.16
7.	0.80	2.065	0.805	100.62	2.80	1.645	2.785	99.46
8.	0.90	2.319	0.899	99.88	3.50	2.045	3.513	100.37

TABLE 4—SIMULTANEOUS DETERMINATION OF CHROMIUM AND IRON IN STAINLESS STEEL

[Wt. of sample—about 5 mg.; Base electrolyte —2MKCl + 3M Triethanolamine + 0.0.1% gelatin; pH 8]

S.S. Sample Nos.	Chromium			Iron		
	Volumetrically, %	Polarographically, %	Error, %	Volumetrically, %	Polarographically, %	Error, %
304	17.94	18.04	+0.56	68.39	68.20	−0.30
316	16.83	16.94	+0.65	69.24	68.13	−1.54
321	17.23	17.00	−1.35	68.44	68.01	−0.63
347	18.26	18.10	−0.90	68.65	68.52	−0.19

recoveries of Cr^{6+} and Fe^{3+} are calculated to be between 98.5 to 101.0 from known values. The results of various polarographic analyses of standard stainless steel samples are presented in Table 4. Polarographic results are further compared with those obtained by standard methods for steel analysis. The individual error for chromium and iron in stainless steel samples have been worked out and found to be within $\pm$ 1.5 per cent and are given in Table 4.

Conclusion

The present polarographic procedure provides a quick and reasonably accurate method for the determination of chromium and iron in a stainless steel solution without their prior separation.

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EDITOR'S NOTE

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A new biuret complex with Cr^{3+} has been prepared. Direct current polarographic and absorption spectral studies by mole-ratio method reveal the formation of a greenish yellow coloured 1:3, [Cr^{3+}-biuret] complex at pH 11.2. The stepwise stability constants of the successive complexes have been calculated by the method of Hume and Deford[1], the values being $K_1=1,800$, $K_2=550$, $K_3=76$ and overall K being 7.5×10^8. The complex compound was observed to have two λ max at 425 mμ and at 600 mμ.

Polarographic and Absorption Spectral Studies on the System [Cr^{3+}-Biuret]

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Introduction

A fairly good amount of evidence for the structure of biuret complexes of bivalent transition metal ions has been derived from solution measurements, apart from numerous spectrophotometric studies, X-ray and infrared spectral measurements that have been reported. Recently, for the first time, polarographic behaviour of biuret at the dropping mercury electrode has been reported by Mishra *et al*[2], and it was observed that biuret molecules coordinate in alkaline media (> 12 pH) through two nitrogens of the amide groups, ionization of two amide hydrogen atoms producing a dianionic ligand, whereas below pH 12, only one amide hydrogen ionizes yielding mono-anionic ligand. In continuation of our earlier studies on the mode of ionization and chelation of biuret, the present paper records observations on the systems biuret-Cr^{3+}.

Tervalent transition metal complexes of biuret have been studied rather scarcely[2–4]. Sanyal[4] & Bour *et al*[3] have reported Ni^{3+} and Cu^{3+} complexes of biuret; Sanyal *et al*[4,5] have reported the infrared spectra of [Co^{3+}-biuret] complex. However, no attempt has so far been made to study the greenish-yellow coloured complex formed with Cr^{3+} and biuret between pH 4.0—11.2. Polarographic (d.c.) and spectrophotometric studies (mole ratio method) reveal the formation of a 1: 3, metal: ligand complex, Cr^{3+} being reduced reversibly with the subsequent addition of increasing concentrations of biuret, at d.m.e., pH 6.4, and constant ionic strength. The stepwise and overall stability constant for the complexation reaction have been evaluated. Obedience of Beer's law has also been recorded.

Experimental

All polarograms were recorded on an automatic recording Cambridge Univector polarograph, employing d.c. polarography. A dipping annulus type cell was used and oxygen-free, dry nitrogen was bubbled through the cell mixture to remove dissolved oxygen. The cell solution was kept in a nitrogenous atmosphere, with the help of a water-seal, during the recording. The height of the mercury reservoir was kept constant throughout. All the measurements were done at 25 ± 0.1°C. The capillary characteristics remained constant throughout the experiment. Mercury pool anode was used throughout these studies.

Stock solutions of various chemicals (A. R. grade) were prepared and used from time to time. Ionic strength of the cell-mixture was kept constant throughout these studies. Only conductivity water was used during all the studies.

pH measurements were carried out on a Philips (model PR 9403) pH meter, which was standardized with potassium hydrogen phthalate (pH=4.0) and ammonia buffer (pH 9.0). The recorded curves have been analysed and plotted on a larger scale.

Absorption spectrum was recorded on a Beckman DU2 model spectrophotometer using a tungsten filament lamp as the source, at medium sensitivity. The cell con-

stant for 1 cm quartz cell used in the experiment was also determined to evaluate the correct value of optical density.

The chromium biuret complex was prepared by mixing 0.1M solution of Cr^{3+} and 0.1M solution of biuret at different ratios. The pH of the solutions was adjusted in each case from 2 to 11. At every ratio of chromium and biuret and at every pH, spectra was obtained by plotting optical densities against wave length. It was observed that complex compound can best be formed at the chromium: biuret ratio 1:3 and pH 11.2 giving two maximum, one at 425 mμ and the other at 600mμ.

Sodium sulphate was added for adjusting pH. At pH 5, 6, 7 a precipitate appeared. Excess hydroxide (30 per cent potassium hydroxide) was added at pH 10-11. While mixing Cr^{3+} and biuret solution in the alkaline medium, precipitate appeared initially but disappeared immediately and a greenish yellow coloured complex was formed. Mole ratio method for the complex was also tried at two different wave lengths for different ratios of [biuret$-Cr^{3+}$] complex using 0.1M solutions, each of which contained a different ratio of chromium to biuret. The total volume was made upto 25 ml. in each case. By plotting optical density against concentration, each solution reveals that optical density increases and then becomes steady at the point where Cr^{3+} to biuret ratio is 1:3. Thus, each mole of Cr^{3+} requires 3 moles of biuret.

The chemicals used in these experiments were all of AnalaR grade. Biuret was recrystallized three times in the laboratory before use.

Results

Chromium^{3+} in 0.1M Na_2SO_4 (pH 6.4) gave two well-defined reversible waves (Fig. 1) having $E\frac{1}{2}$$-1.6$V and -1.84V respectively. The first wave corresponds to reduction of Cr^{3+} to Cr^{2+} and the second one to the reduction of Cr^{2+} to Cr-Hg amalgam. However, the height of second wave (a two-electron process) is not exactly double that of the first wave (one-electron process) due to hydrogen evolution. On adding increasing concentrations of biuret to a chromium^{3+} solution in sodium sulphate medium (pH 6.4), the $E\frac{1}{2}$ of the first wave was observed to shift towards more negative potentials indicating complexation of biuret with Cr^{3+}. This was further supported by the decrease in i_d with increasing amounts of biuret, in the cell (Table 1).

On plotting [$-\log$ (C)] of biuret against $E\frac{1}{2}$, a *straight line was obtained having a slope* 0.02, indicating thereby the formation of 1:3 complex involving a three-electron change. The process was found to be reversible.

TABLE 1—POLAROGRAMS OF 8.19×10^{-4} M Cr^{3+} IN 0.1M, Na_2SO_4 WITH INCREASING CONCENTRATIONS OF BIURET

Sl. No.	Conc. of Biuret Added, M	$E\frac{1}{2}$, volts	i_d, μA	Remarks
1.	1.585×10^{-3}	-1.6810	0.87	
2.	2.000×10^{-3}	-1.6850	0.35	
3.	2.520×10^{-3}	-1.6895	0.80	Complexation
4.	3.270×10^{-3}	-1.6950	0.72	indicated
5.	4.465×10^{-3}	-1.7000	0.60	
6.	6.550×10^{-3}	-1.7050	0.60	
7.	6.690×10^{-3}	-1.7075	0.59	
8.	8.900×10^{-3}	-1.7125	0.55	
9.	8.900×10^{-3}	-1.7175	0.53	

Absorbance Studies: Two methods were employed in an attempt to establish a mole ratio for the chromium complex in solution. These were the method of Yoe and Jones[6] (the mole ratio method) and the Vosburgh-Cooper's[7] method. The mole ratio method also gave a 1:3, metal: ligand stoichiometry. The method of continuous variation did not give fruitful results due to precipitation of Cr $(OH)_3$, when Cr^{3+} was in excess. Application of Vosburgh-Cooper's method revealed the nature of the complex, no isosbestic point was observed,

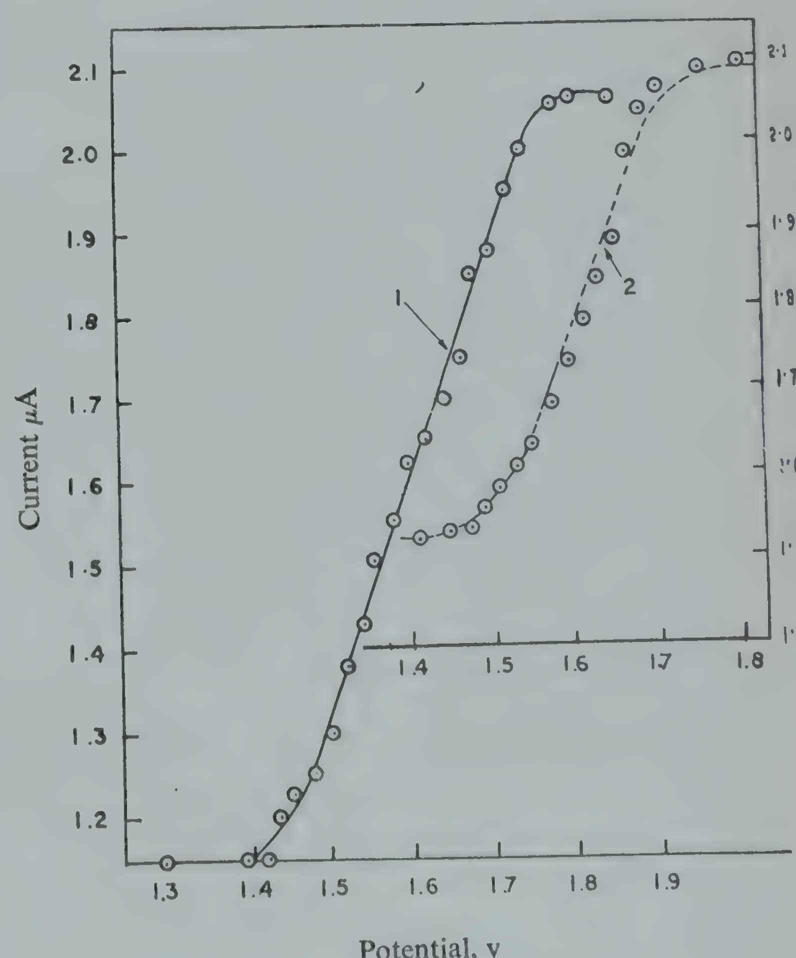


Fig. 1—Polaragrams

1. (8.19×10^{-3}M) Cr^{3+}
2. Cr^{3+}+(9.83×10^{-3}M) Biuret

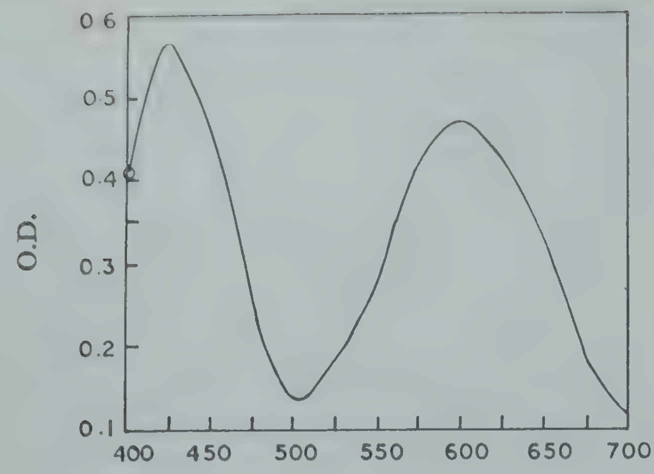
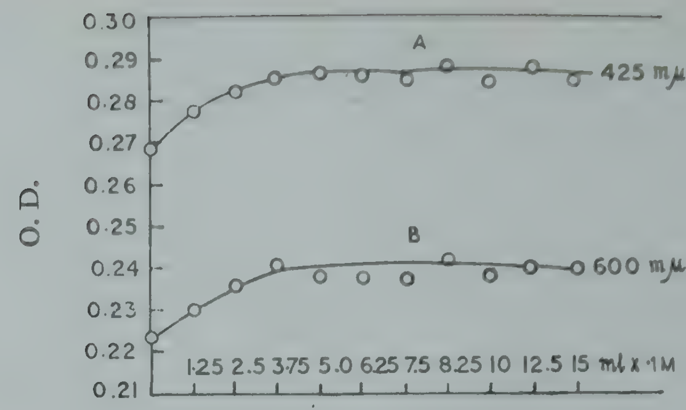


Fig. 2—Absorption Spectrum of Chromium-Biuret Complex at pH 11.2



Biuret Mol./Mol of Cr^{3+}

Fig. 3—Mole Ratio Studies on Chromium-Biuret Complex

indicating formation of only one complex. The chrome-alum showed considerable absorbance at the wave lengths of the maximum absorbance of the [Cr^{3+}-biuret] complex, so that blank sets of observations for chromium^{3+} solutions were carried out at different concentrations; these were utilized to introduce the necessary corrections in absorbance values for the complex.

The complex (solution) was observed to have two λmax, at 425mμ and at 600 mμ, (Fig. 2). The mole-ratio method indicated the formation of a 1:3, metal: ligand complex as is evident from Fig. 3, each mole of chromium^{3+} requiring three moles of biuret.

Studies on variation of pH showed that the complex formation takes place between pH 4.00-11.2 but maximum intensity was observed at pH 11.2. The order of addition of reagents for the colour development had no effect on the intensity. Beer's law is obeyed between 100-200 ppm of Cr^{3+} concentration.

Discussion

It is evident from the shift in $E_{\frac{1}{2}}$ of Cr^{3+} wave towards more negative potentials on subsequent addition of increasing amounts of biuret, along with subsequent decrease in i_d that Cr^{3+} is reduced at the dropping mercury electrode. The slope of the plot (log of biuret) Vs $E_{\frac{1}{2}}$, 0.02V, indicated a 1:3 complex involving three electron processes. The 1:3, Cr^{3+}: biuret stoichiometry is also evinced from the mole-ratio method (of absorption studies), each mole of Cr^{3+} requiring three moles of biuret (Fig. 3).

The stepwise stability constants of the complex were evaluated by the method of Hume and Deford[1]. The successive formation functions were evaluated by making use of the following equations[1].

$$\text{(i)}\quad F_0[x] = \sum \frac{k_j\, C_x^J\, f_x^J}{f_{Mxj}} = \text{antilog}\left\{ 0.435\, \frac{nF}{RT} [(E_{\frac{1}{2}}^{o})_s - (E_{\frac{1}{2}})_c] + \log \frac{I_s}{I_c} \right\}$$

TABLE 2—Evaluated Formation Functions and the Overall Stepwise Stability Constant

Sl. No.	Concn. of Biuret, mM	$E_{\frac{1}{2}}$, V	F_0 (x)	F_1 (x)	F_2 (x)	F_3 (x)	$K = K_1K_2K_3$
1.	1.585	−1.6810	2.775	1,119.0	429.6	75.3	—
2.	2.000	−1.6850	3.007	1,003.0	398.5	75.7	—
3.	2.520	−1.6895	3.253	894.1	359.1	75.6	K_0=1.0
4.	3.270	−1.6950	3.572	786.5	309.9	42.8	—
5.	4.465	−1.7000	3.888	636.9	258.2	42.9	K_1=1,800
6.	6.550	−1.7050	4.233	493.7	199.4	53.5	K_2=550
7.	6.690	−1.7075	4.416	510.7	192.7	53.4	K_3=76
8.	8.900	−1.7225	4.806	427.0	154.2	44.4	$K=7.5 \times 10^8$
9.	9.830	−1.7175	5.232	430.4	139.3	41.7	—

Further structural investigations relating to a molecular formula evaluation are in progress.

(ii) $$F_1[x] = \frac{\left[F_0(x) - \frac{k_0}{f_s}\right]}{C_x f_x} \text{ where } K_0 = \frac{k_0}{f_s} = 1$$

(iii) $$F_2[x] = \frac{\left[F_1(x) - \frac{k_1}{f_{Mx}}\right]}{C_x f_x}$$

In Table 2 are summarized the evaluated formation functions along with the overall log K and the stepwise stability constants.

Acknowledgement

The authors are thankful to Dr. B. K. Banerjee, Superintendent, Physical Research Wing, for encouragement.

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The effect of MnO_2 and MgO additives on the self-disintegration and inversion characteristics of the dicalcium sillicate (C_2S) clinker up to 1550°C has been studied with particular reference to the nature of atmosphere during heat treatment conditions. It has been observed that disintegration tendency of clinker is retarded gradually with increasing amount of MnO_2 and reverse is the case with MgO. Again reducing atmosphere favours disintegration of clinker doped with MnO_2 whereas with MgO it is retarded. When both MnO_2 and MgO are present in clinker, disintegration is not observed in oxidising condition. In general disintegration occurs at lower temperature (320-350°C) in case of clinker with these additives than that of pure clinker (525°C). The data obtained establishes a workng limit of crystalline solubility of Mn in dicalsium silicate and effect on the onset of disintegration. The temperatures of the various inversions from α to γ form of C_2S are influenced by these additives. The mechanism for the onset and limit of disintegration of these systems have been suggested from these high temperature inversion characteristics.

Effect of Additives on the Self-Disintegration of Dicalcium Silicate Clinker

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Introduction

The phenomenon of dusting without the help of mechanical energy due to β-γ inversion of dicalcium silicate finds a noble application in the method of producing silicates in the form of powder from dicalcium silicate clinker or slags containing dicalcium silicate[1]. Soil-conditioner in fine powder form rich in P_2O_5 has been prepared from basic open-hearth slags in Czechoslovakia by this self-disintegration process[2]. Recent work reveals that dusting of dicalcium silicate occurs solely

by the inversion of β' into γ and its onset occurs commonly at 525°C in an undercooled stage. β' is a metastable phase and inverted from β at 670°C[3]. But various cations even if present in small amounts inhibit this transition of dicalcium silicate which causes self-disintegration of the solid silicate mass. Of these, mention may be made of Mn, P, As, Sb, V, Ba, Sr, Zn, Cr, W. Mo, Ti and B[4].

Nurse[5] found that Mn if present in higher oxidation level, i.e. in heptavalent state inhibits the β'-γ transition of dicalcium silicate, but if present as bivalent form does not have any influence on this transition.

Magnesium, on the other hand, can enter into the lattice of dicalcium silicate, the range of limiting solubility in α-α' form has been worked out by Schlaudt and Roy[6]. However the role of Mg on the β'-γ transition of dicalcium silicate and its dusting phenomena has not been studied in detail.

Indian basic slags usually contain manganese in large proportion[7] (4.45 per cent as MnO_2). Besides, Mg is also present as MgO (12.20 per cent as MgO) in these slags. The phase diagram of dicalcium silicate containing mixed elements like Mg and Mn and also its dependence on the nature of atmosphere of heat treatment have not so far been studied in detail[8]. In order to develop a process know-how for preparing dicalcium silicate powders from Indian slags, the behaviour of dicalcium silicate transformation in presence of other constituents, particularly of Mn and Mg should be clearly known.

The present work is sought to determine the critical role of Mn and Mg both separately as well as mixed form on the dusting of dicalcium silicate in oxidising and reducing conditions and their inversion characteristics during cooling.

Experimental

The following systems were taken for the present investigation:

(i) $2CaO-SiO_2-MnO_2$ or $C_2S^*-MnO_2$
(ii) $2CaO-SiO_2-MgO$ or C_2S^*-MgO
(iii) $2CaO-SiO_2-MnO_2-MgO$ or $C_2S^*-MnO_2-MgO$

Preparation of batch: In each system lime (CaO) and silica (SiO_2) contents were maintained in the stoichiometric ratio to form dicalcium silicate and only the amounts of additives, e.g. MnO_2 & MgO, were varied. Ingredients used were quartz powder (—200 mesh) of purity 99.7 per cent SiO_2 and analar quality $CaCO_3$ (for CaO), manganese dioxide and magnesium oxide were used for this investigation.

*(C = CaO and S = SiO_2)

First of all mixture of quartz and $CaCO_3$ powders having the stoichiometric composition of CaO and SiO_2 in the ratio of 2:1 was prepared, for each experiment 10 gm of this mixture was taken and to it MnO_2 was added in different quantities starting from 1 upto 13 per cent by weight of C_2S mixture. Similarly MgO was also added with each 10 g. of the stoichiometric mixture in different quantities starting from 3 upto 23 per cent by weight. A few similar batches were prepared by adding both MnO_2 and MgO together in different amounts such as 1-1, 5-5, 9-9, 11-11, 12-12 and 13-20 p.c. respectively. The composition of C_2S-MnO_2 and C_2S-MgO and C_2S-MnO_2-MgO system for every experiment studied are shown in the diagrams 1, 2 and 3 respectively.

Heat Treatment of the Batch: Each batch was subjected to heat treatment separately both in reducing as well as oxidising atmosphere. In each atmosphere, the sample was heated at 1550° ± 10°C for ½hr. For reducing and oxidising condition a high temperature carbon resistance and a silicon carbide tube furnace respectively were used. Both heating and cooling were done inside the furnace. Time required to raise the desired temperature and cooling down to room temperature was 2½ hr. approximately in each case. The sintering state of each sample was examined visually at maximum heating temperature and it was found that each sample sintered to hard mass at this temperature. Also each heat treated product after cooling down to room temperature was examined visually and the limit and tendency of disintegration were recorded. These observations for C_2S-MnO_2, C_2S-MgO and C_2S-MnO_2-MgO systems are shown in their respective composition diagrams, separately in oxidising as well as reducing atmosphere.

Differential Thermal Analysis (DTA): DTA of some selected samples was done in the Linseis fully automatic DTA unit using platinum cylinders as sample holders and Pt-Pt/Rh (13 per cent) as thermocouples. Each sample was heated upto 1550°C in a similar way as heat treatment operation made for disintegration experiments and subsequently cooled down to room temperature. Only the cooling thermograms are recorded in the Figs. 4, 5 & 6. The rate of cooling was maintained at 10°C/min. approximately. Ignited alumina was used as reference substance.

X-ray Diffraction Analysis: X-ray diffraction photographs of a few selective samples of all the systems C_2S-MnO_2, C_2S-MgO and C_2S-MnO_2-MgO were taken in a Guinear-De-Woulff focussing type of camera utilising CuK α radiation generated at 40 KV and 20 mA.

The time of exposure in each case was eight hours. The different phases present as identified from the photographs are shown in Table 1.

Results and Discussion

It is evident from Figs. 1 & 2 that the tendency and the limit of disintegration of dicalcium silicate are very much affected by additives e.g. MnO_2 and MgO. The disintegration tendency of C_2S containing MnO_2 is retarded gradually with increasing amount of MnO_2 until it is completely stopped at 9 to 11 per cent depending upon atmospheric condition. Disintegration is only partial with 6 to 9 per cent MnO_2. Reverse is the case with MgO as additive. Disintegration of C_2S is never stopped as observed with MgO from 3 to as high as 23 per cent. It is complete upto 7 per cent MgO and may be complete or partial with higher quantity of MgO depending upon the atmosphere of heat treatment.

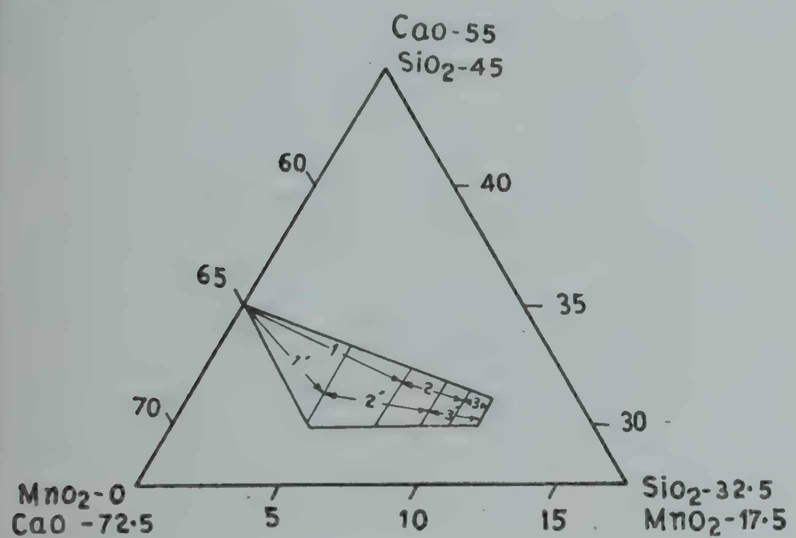

Fig. 1—Composition Diagram of C_2S-MnO_2 System Showing Limits of Disintegration

1,1′ —Represent complete disintegration zone
2,2′ —Represent partial disintegration zone
3,3′ —Represent no disintegration zone
1,2,3 —Represent oxidizing condition zone
1′2′3′ —Represent reducing condition zone

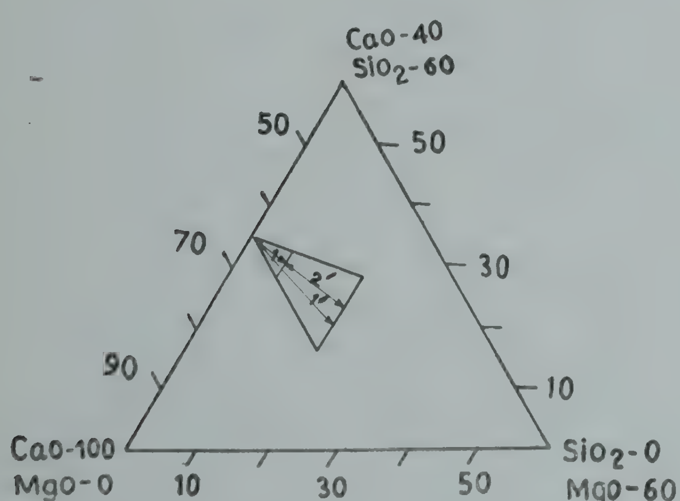

Fig. 2—Composition Diagram of C_2S-MgO System Showing Limits of Disintegration

1,1′ —Represents partial disintegration zone
2′ —Represents partial disintegration zone
1 —Represent oxidizing condition
1′,2′ —Represent reducing condition

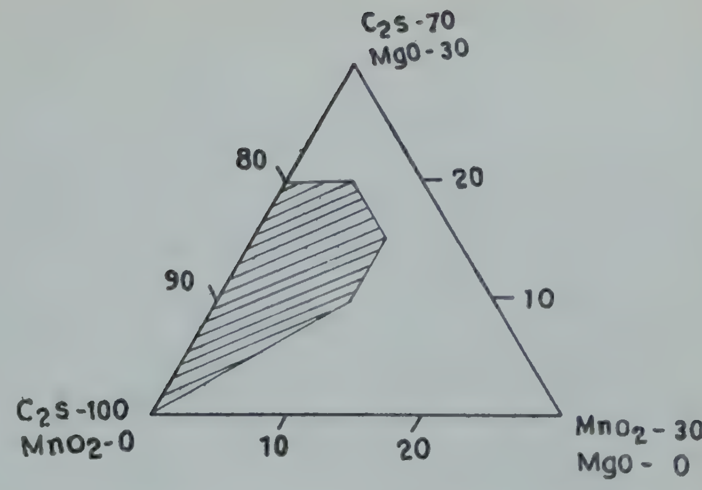

Fig. 3—Composition Diagram of C_2S-MnO_2-MgO System
(Shaded portion represents no disintegration zone in oxidizing atmosphere and partial disintegration zone in reducing atmospheric.)

In case of C_2S containing either MnO_2 or MgO only limit of disintegration has been affected by the atmosphere of heat treatment. For example, C_2S containing MnO_2 upto 8 per cent disintegrates completely and that from 9-11 per cent partially in reducing atmosphere whereas that containing upto 5 per cent completely and 6 to 9 per cent partially in oxidising condition. Again C_2S containing MgO from 3 to 23 per cent disintegrates completely in oxidising condition, whereas it does so upto 7 per cent MgO in reducing condition, beyond which the disintegration has been found to be only partial. When these two additives are present in combination the disintegration tendency is influenced drastically, by the atmosphere of heat treatment (Fig. 3). In reducing condition C_2S containing MnO_2 and MgO upto as high as 13 & 20 per cent respectively disintegrates partially whereas there is no disintegration in oxidising condition.

Nurse[7] observed that two exothermic peaks at 1427°C and 670°C appear in the cooling curve of pure C_2S. These two peaks have been confirmed and thought due to α-β and β-β' inversion of C_2S. But later work revealed that the former peak is due to α-α' inversion of C_2S. Moreover one exothermic hump (distrubed zone in the thermogram) is also observed at 525°C which represents β'-γ inversion and onset of disintegration. No peak due to α'-β inversion appears in the thermogram. From the DTA cooling curves (Figs. 4, 5 & 6) it is evident that all these peaks are present in those samples which disintegrate either completely or partially. Although DTA

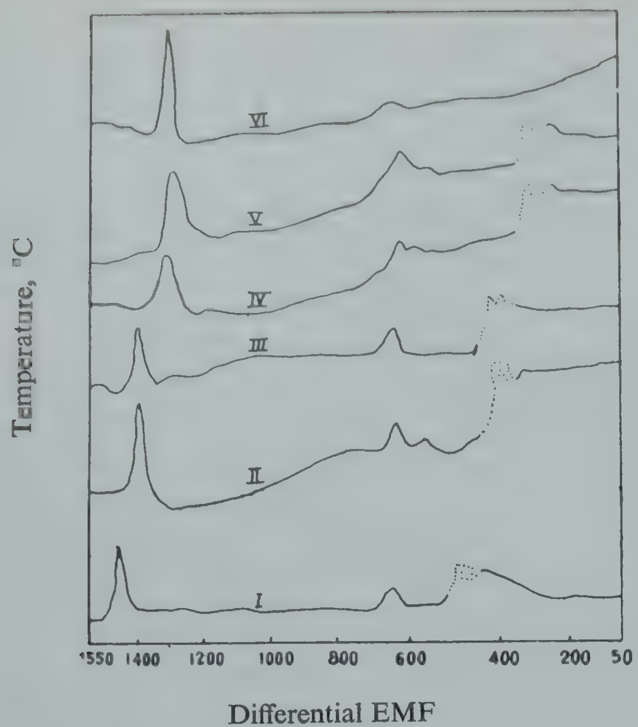

Fig. 4—DTA Cooling Thermograms of C_2S-MnO_2 System
[I, II, III, IV, V & VI represent C_2S containing 0, 1, 3, 5, 7 and 11 per cent MnO_2 respectively.]

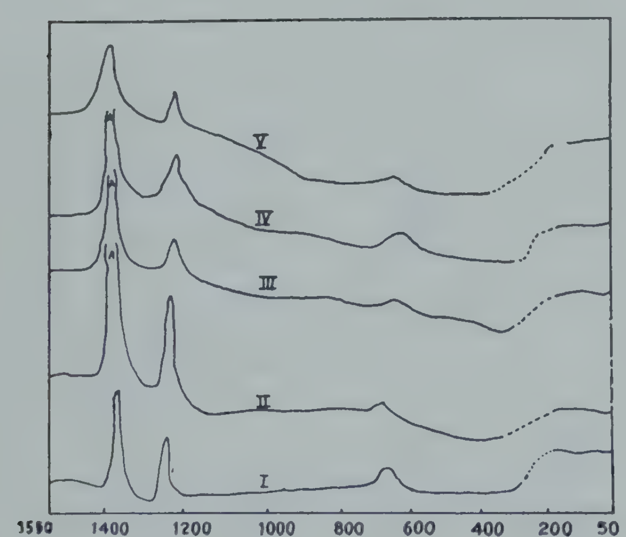

Fig. 5—DTA Cooling Thermograms of C_2S-MgO System
[I, II, III, IV & V represent 1, 5, 9, 15 & 23 per cent MgO respectively.]

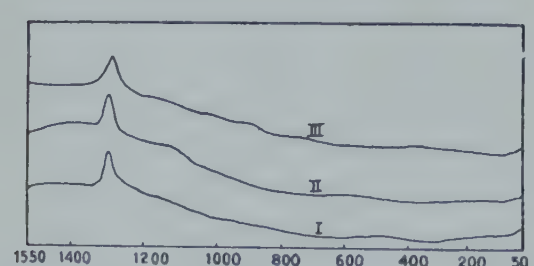

Fig. 6—DTA Cooling Thermograms of C_2S-MnO_2MgO Systems
[I, II & III represent C_2S containing MnO_2 & MgO 1-1, 11-11 & 13-20 per cent respectively.]

results have been obtained in similar oxidising condition of heat treatment only, an examination over the sequence of the inversion of dicalcium silicate as observed in the DTA cooling thermogram containing additives throws some interesting light on the mechanism of their disintegration. In case of C_2S containing MnO_2, α-α' and β-β' inversion temperatures gradually decrease to 1300°C and 630°C respectively with increasing MnO_2 content upto 9 per cent. The onset of disintegration is also lowered down to 350°C, but beyond 9 per cent this peak is absent (Fig. 4). In oxidising condition Mn will exist in higher oxidation form and enter easily in the anionic position. It seems that Mn can go upto 9 per cent as MnO_2 in this position of C_2S lattice. According to Nurse[5] Mn in MnO_4^- state inhibits the β'-γ transition of dicalcium silicate and if Mn is present as Mn_2SiO_4 along with C_2S it does not have any influence on this transformation. The occurrence of disintegration of dicalcium silicate upto 9 per cent of MnO_2 in oxidising condition is therefore due to its substitution upto maximum limit of crystalline solution. In reducing condition, Mn is reduced to lower oxidation form such that its maximum limit of crystalline solutiion is not reached even if the system contains MnO_2 beyond 9 per cent. The disintegration of C_2S containing MnO_2 as high as 11 per cent is thus possible in such condition. It is interesting to mention here that no Mn compound has been identified by x-ray diffraction method as free phase even in the disintegrated mass obtained in reducing condition (Table 1). It may so happen that Mn_2SiO_4 so formed remained in glassy state which could not be detected by x-rays.

Mg also enters in the cationic position of dicalcium silicate. Schlaudt[6] *et al* observed that limiting solubility of MgO in C_2S is 1.59 per cent. The α-α' inversion temperature decreases with increasing substitution down to 1400°C for the maximum crystalline solution. In case of C_2S containing MgO system two exothermic peaks at 1390°C and 1250°C appears in the cooling thermogram of each composition. Evidently the first peak is due to α-α' inversion of this crystalline solution which has been developed as the composition in the system always exceeding the critical composition of this solid solution. Further Toropov[9] *et al* observed that α'-β' inversion occurs at 1230°C in C_2S solid solution containing MgO. The peak therefore represents this inversion. Two other exothermic peaks at 600°C and 320°C also appear in their cooling curve, evidently these are due to β-β' inversion and onset of disintegration respectively. From the DTA thermograms it is evident that all the inversion temperatures are unaffected by the quantity of MgO in C_2S system (Fig. 5).

TABLE 1—PHASES IDENTIFIED BY X-RAY DIFFRACTION METHOD IN THE HEAT-TREATED SAMPLES

System	Additive and its p.c. by wt.	Treatment in Reducing Atmosphere		Treatment in Oxidizing Atmosphere	
		Disintegration tendency	Phases identified	Disintegration tendency	Phases identified
C_2S	—	Complete	γ-C_2S—Major β-C_2S—Trace	Complete	γ-C_2S
C_2S-MnO_2	MnO_2—5	—	—	Complete	γ-C_2S—Major β-C_2S—Trace
	MnO_2—6	Complete	γ-C_2S—Major β-C_2S—Trace	—	—
	MnO_2—7	—	—	Partial	γ-C_2S—Major β-C_2S—Minor
	MnO_2—9	Partial	γ-C_2S—Major β-C_2S—Minor	—	—
	MnO_2—11	—	—	Nil	β-C_2S & γ-C_2S both appreciable
	MnO_2—12	Nil	β-C_2S & γ-C_2S both appreciable	—	—
C_2S-MgO	MgO—5	—	—	Complete	γ-C_2S—Major β-C_2S—Trace Merwinite & Periclase—trace
	MgO—7	Partial	γ-C_2S—Major β-C_2S—Trace Merwinite & Periclase—trace	—	—
	MgO—11	—	—	Complete	γ-C_2S—Major β-C_2S & Merwinite—trace Periclase—Minor
	MgO—13	Partial	γ-C_2S—Major β-C_2S—Minor, Merwinite & Periclase—trace	—	—
	MgO—21	Partial	γ-C_2S—Major β-C_2S—appreciable Merwinite—trace Periclase—appreciable	Complete	γ-C_2S—Major β-C_2S—appreciable Merwinite—trace Percelase—appreciable
C_2S-MnO_2-MgO	MnO_2-MgO 1:1	Partial	γ-C_2S—Major β-C_2S—Trace Merwinite—trace	Nil	γ-C_2S—Major β-C_2S—Trace Merwinite—trace
	MnO_2 : MgO 13:20	Partial	γ-C_2S—Major β-C_2S—Minor Periclase—Appreciable Merwinite—Trace	Nil	γ-C_2S—Major Merwinite—Minor β-C_2S—Trace Periclase—appreciable

X-ray study reveals that besides γ-C_2S some merwinite and periclase are present in all their disintegrated mass (Table 1). Periclase increases with increasing concentration of MgO in the C_2S system. Both the merwinite and periclase grains are larger in reducing condition than the oxidising one. The apparent partial disintegration of C_2S containing higher proportion of MgO in reducing condition may be due to the growth of these larger crystals which exist in the form of chips not broken by the pressure released due to β'-γ transition of C_2S. It may therefore be inferred that the crystalline solution of α-C_2S with 1.59 per cent MgO coexists with merwinite and periclase during formation of C_2S which ultimately inverts to γ-form causing disintegration. The onset of disintegration is lowered down to 320°C as a result of magnesium substitution.

In the C_2S system containing both MgO and MnO_2 no peak other than α-α' inversion at 1310°C is present in

the cooling curve (Fig. 6). This lowering of inversion temperature is evidently due to the combined substitution effect of both Mn and Mg in the anionic and cationic position of C_2S respectively. It may be mentioned here that predominantly β-C_2S has been detected in samples of oxidising heat treatment condition and γ-C_2S in reducing condition (Table 1).* From the observation it appears that when magnesium is present in cationic position, the maximum solubility of higher valent Mn in C_2S lattice is lowered appreciably and beyond the critical limit the onset of disintegration does not occur. Furthermore, in appropriate reducing condition the Mn in this lattice position can be maintained below the critical limit even when the overall manganese content of this system is as high as 13 per cent.

Acknowledgement

Thanks are due to Dr. B. K. Banerjee, Additional Superintendent of this Division, for his encouragement during this investigation.

* X-ray diffraction patterns of β' & β are almost similar. No attempt has been made to decipher these two phases in the present context.

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When $(MoO_4)^{2-}$ ions are added to soils variable amounts of molybdenum are retained the retention of which is found to be conditioned by $CaCO_3$, and organic matter contents of soil. Calcium carbonate helps in increasing retention value. The removal of organic matter brings about a decrease of 16.83 to 25.91 per cent in the retention values of Mo in original soils.

Molybdenum Retention in Soils in Presence of Free Iron Oxide and Calcium Carbonate

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The retention of molybdenum cannot be studied in its cationic form as it is mostly in anionic form i.e. molybdate. Ammonium and sodium molybdates are the common soluble salts of molybdenum. It is believed that plants are able to utilise only molybdate ions from soil solution. The retention of molybdenum by soil has been studied by a number of workers and it has been found to depend upon a number of conditions, such as, con-

centration of solution, pH of soils, presence of $CaCO_3$ in soils and removal and additions of iron oxide from soils[1-5].

As no data on the retention of molybdenum in Indian soils are available hence it was thought proper to investigate the retention of molybdate ions in three soils—black, red and alkali soils of eastern Uttar Pradesh.

Experimental

For studies on molybdenum retention, seven representative surface samples comprising of 3 black soils, 2 red soils and 2 alkali soils were selected. A description of their location and some important chemical characteristics are given in Table 1.

20 ml of ammonium molybdate solution was added to 2 g. soil samples. The contents were shaken for one hour and were then allowed to remain in contact for 18 hours. Next day, the supernatant liquid was separated by filtration using suction. The filtrate was analysed for molybdenum content as described by Jackson[6].

The difference between the amounts of the molybdenum initially added and the amounts present in the filtrates was taken to be the amount of molybdenum retained by 2 g. of soil. It has been represented by a notation R. The amount of Mo present in the blanks was also deducted in all the experiments.

(i) *Effect of Concentration*: 2 g. samples of black, red and alkali soils were shaken in conical flasks with 20 ml ammonium molybdate solution so as to add 10, 15 and 20 ppm molybdenum and the amount of molybdenum retained was determined after 18 hours by the method given above. The results obtained are given in Table 2.

(ii) *Effect of Carbonates on Molybdenum Retention*: In order to find out the role of increasing doses of insoluble carbonate on molybdenum retention, varying amounts of calcium carbonate (1, 2 and 4 per cent) were mixed with 2 g. soil. 20 ml of ammonium molybdate solution (containing 10 ppm Mo) was added and the amount of Mo retained was estimated as given before. The results obtained are presented in Table 3.

(iii) *Effect of Removing and Adding Iron Oxide on Molybdenum Retention*: Iron oxide from one sample each of black (Babuganj), red (Meja) and alkali (Soraon-2) soils was removed by sodium dithionite-citrate-bicarbonate method[7] by taking 20 g. of the soils. Molybdenum retention was determined by taking 2 g. of the iron-free soil by the method described before.

Freshly prepared hydrated iron oxide was also added to these samples at the rate of 4 and 8 per cent and then Mo retention was studied as before. The results obtained are given in Table 4.

Results and Discussion

(i) *Effect of Concentration*: As the concentration of added Mo is increased (Table 2) the amount of molybdenum retained (R value) by the soils increases. The black soils from Babuganj and Gaipura are the two exceptions to this generalization at 15 ppm. However, at 20 ppm. many of the soils do not exhibit increasing trend. On an average basis, red soils show highest re-

TABLE 1—LOCATION AND CHEMICAL CHARACTERISTICS OF SOILS

Soils	Name of Place (District)	pH	Sesqui-oxide, %	Total Carbonates as $CaCO_3$, %	Organic Carbon, %	Total Mo, ppm.
Black Soil	Babuganj (Allahabad)	7.5	16.72	2.75	0.40	2.37
,, ,,	Birha (Allahabad)	8.7	4.72	0.80	0.15	0.87
,, ,,	Gaipura (Mirzapur)	7.6	20.62	2.72	0.52	1.62
Red Soil	Meja (Allahabad)	7.5	7.60	1.45	0.60	3.00
,, ,,	Sukrit (Allahabad)	7.7	10.00	1.25	0.90	2.62
Alkali Soil	Soraon-1 (Allahabad)	9.0	—	11.00	0.24	1.50
,, ,,	Soraon-2	7.9	—	1.07	0.58	1.25

TABLE 2—EFFECT OF CONCENTRATION ON MOLYBDENUM RETENTION BY SOIL

Soils	Molybdenum Added as Ammonium Molybdate					
	10 ppm		10 ppm		20 ppm	
	R	per cent Mo retained	R	per cent Mo retained	R	per cent Mo retained
Black Soils						
Babuganj	6.50	65.00	6.00	40.00	7.50	37.50
Birha	5.75	57.50	6.00	40.00	6.50	32.50
Gaipura	7.00	70.00	10.75	71.60	9.75	48.75
Average	6.41	64.16	7.58	50.53	7.19	39.58
Red Soils						
Meja	8.75	87.50	13.75	91.70	18.00	90.00
Sukrit	10.00	100.00	14.75	98.33	14.25	71.25
Average	9.37	93.75	14.25	95.02	16.13	80.63
Alkali Soils						
Soraon-1	9.75	97.50	14.50	96.60	15.75	78.75
Soraon-2	2.75	27.50	7.00	46.67	6.00	30.00
Average	6.25	62.50	10.75	71.63	10.87	54.38

TABLE 3—EFFECT OF ADDING CALCIUM CARBONATE ON MOLYBDENUM RETENTION BY SOILS

(Mo added @ 10 ppm.)

Soils	Control	% Calcium Carbonate Added		
		1.00	2.00	4.00
Black Soils				
Babuganj	6.50	4.25	6.50	9.75
Birha	5.75	8.00	7.25	9.75
Gaipura	7.00	6.50	7.00	7.25
Average	6.41	6.25	6.91	8.91
Red Soils				
Meja	8.75	8.75	8.75	9.00
Sukrit	10.00	10.00	10.00	10.00
Average	9.37	9.37	9.37	9.50
Alkali Soils				
Soraon-1	9.75	6.50	8.00	8.00
Soraon-2	2.75	4.25	7.25	8.75
Average	6.25	5.37	7.62	8.37

TABLE 4—EFFECT OF IRON OXIDE ON MOLYBDENUM RETENTION BY SOILS

(Mo Added @ 10 ppm.)

Soils	Control	Iron-free Soil + 10 ppm Mo	Iron-free Soil + 4% Fe_2O_3 + 10 ppm Mo	Iron-free Soil + 8% Fe_2O_3 + 10 ppm Mo
Black Soil				
Babuganj	6.50	0.50	4.50	1.50
Red Soil				
Meja	8.75	0.00	8.50	1.00
Alkali Soil				
Soraon-2	2.75	2.00	1.00	1.00

tention of Mo and the black soils the least and the alkali soils stand midway, thus the order is

red soils > alkali soils > black soils.

At 10 ppm R values range from 27.5 to 100 per cent of added Mo but at 20 ppm. the lower limit rises to 30 per cent. It is only the black soils that exhibit least R values i.e. they appear to saturate themselves quickly.

A high percentage of molybdenum retained by red soils points to a possibility of Mo being precipitated. Such a variability in molybdenum retentive capacity (MRC) of these soils, thus appears to be characteristic of the soil types collected from different places. The red soils possess a high Mo retaining capacity. It is also clear that 10 ppm can be chosen as a safe and reasonable concentration of Mo at which retention studies can be further pursued. It is on this assumption that a level of 10 ppm Mo has been used throughout the studies reported hereafter.

(ii) *Effect of Calcium Carbonate Addition*: From the above results, it is observed that there is an increase in molybdenum retention with increased addition of $CaCO_3$ to black, red and alkali soils (exception alkali soil of Soraon-1). The increases are, however, very marked in all the black soils and in one of the alkali soils, there being no change in the case of red soils, even at highest level of $CaCO_3$ addition. This is an exceptional case.

(iii) *Effect of Iron Oxide on Molybdenum Retention*: The results obtained (Table 4) clearly demonstrate the role of iron oxide in controlling the retention of added Mo. On removing iron oxide, the R values are markedly lowered (even zero in red soil). However, when 4 per cent hydrated iron oxide is added to those iron-free soils, the values increase considerably in black and red soils (but they decrease in alkali soils). On further increasing the dose of iron oxide the values decrease. This is a peculiar behaviour and it points out that iron oxide does not so much regulate Mo retention at high contents of iron oxide in soils as at lower contents and hence the decrease in R value as a result of the removal of iron oxide may not be solely due to this factor but due to changes in the chemical and physical properties of soils as a result of the drastic treatment adopted for the removal of iron oxide from soils.

Acknowledgement

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A new and quick a.c. polarographic method with negligible interference has been developed for estimation of as low as 1 ppm of managnese in calcite.

Polarographic Determination of Manganese in Calcite

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The conventional polarographic determination of micro amounts of manganese in different materials involves manifold problems. Difficulty is encountered when a solution, having a more readily reducible major constituent, such as iron, than the minor constituent, e.g. manganese, is to be determined. Frequently, a time-consuming chemical or electrochemical separation[1,2] has to be carried out before the minor constituent is determined polarographically. Such separations often lead to a poor accuracy due to losses and impurities introduced during the separations. Another disadvantage of the conventional method is in its poor resolving power, unless the half-wave potentials differ by at least 100 mV, it is difficult to measure with accuracy the heights of individual waves (viz. those of Ni^{2+} and Mn^{2+}).

However, detection and determination of small amounts of manganese in the Indian calcite can yield useful information on various genetic problems[3] and on the location of the deposit from which they originated. A given mineral, e.g. calcite, although found in different locations, has a characteristic association of the label elements dispersed in trace concentration. Manganese, for instance, is usually associated with the Indian calcite. The present paper records observations on a new a. c. polarographic method for the estimation of manganese down to 1 ppm, the main advantage being that it is quick with negligible interference.

Experimental

Stock solutions of lithium and manganese chlorides, prepared from A. R. grade chemicals, were used throughout. A freshly prepared solution of 0.005 per cent gelatin was used to suppress the maxima during the recordings of conventional polarograms. Only conductivity water was used throughout these studies and the strength of the medium was kept constant throughout.

Polarograms—a. c. as well as d.c.—were recorded on an automatic recording polarograph* using d.m.e. and mercury pool anode. The characteristics of the capillary were as follows: $m = 1.042$ mg./sec. $t = 4.4$ sec. The capillary characteristics remain unaltered throughout these studies; the counter and compensation currents were nil and damping was 3 throughout. Oxygen-free, dry nitrogen was bubbled through the cell solution to drive off dissolved oxygen and during all the recordings the cell solution was kept in a nitrogenous atmosphere $i_d/\sqrt{h}$ was found to be constant—h being the height of mercury reservoir—indicating thereby a diffusion controlled process suitable for analytical purposes.

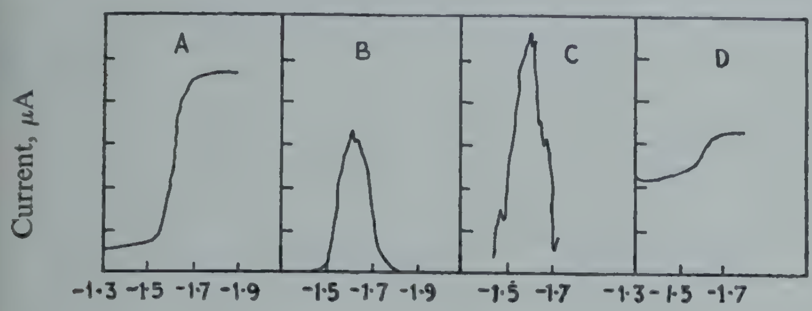
Sample Treatment: A weighed amount of the sample —*ca* 1 g.—was dissolved in 5 ml. of nitric acid (conc.) and evaporated to dryness, then 5 ml. of hydrochloric acid (conc.) was added to it and again evaporated to dryness. Treatment with nitric acid is essential to dissolve any manganese dioxide present in the calcite. The residual mass was again treated with 5 ml. of hydrochloric acid (conc.) and evaporated to dryness, extracted with water, filtered and made up to volume.

Results and Discussion

In 0.1M aqueous lithium chloride, Mn^{2+} gives[2] a well-

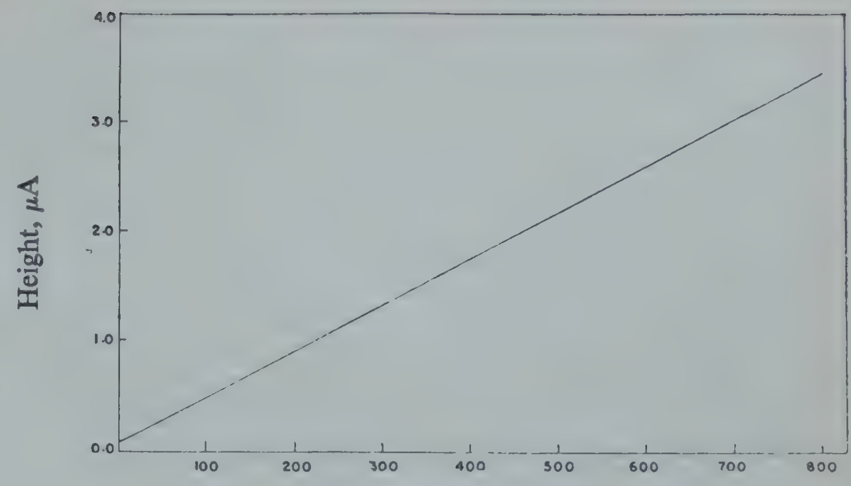
* Cambridge Univector

defined d.c. polarographic step with $E_{\frac{1}{2}} = -1.6$ volts (Fig. 1, Curve A). But Ni^{2+}, Fe^{2+} and Fe^{3+} are to be separated before recording the Mn^{2+} step because of interference from these ions even if present in traces. Moreover, the minimum amount of Mn^{2+} determined was around 200 ppm.



Potential, volt
Fig. 1

However, in the 0.1M aqueous lithium chloride, Mn^{2+} gave a well-defined a.c. polarographic step with E_{max}—1.6 volts (Fig. 1, Curve B). Mn^{2+} concentration of 1 ppm. in the cell solution too yields (Table 1) a well-defined a.c. polarograph step with $E_{max} = -1.6$ volts. Moreover, Zn^{2+} and Ni^{2+} steps are well separated



Manganese, ppm
Fig. 2

magnetic spectra (Ghosh, P. K., *Private Communication*).

Interference: Fe^{2+}, Cr^{3+}, Fe^{3+}, Al^{3+} and Mg^{2+} do not interfere even if present upto 500 ppm. Cu^{2+}, Zn^{2+}, V^{2+}, Ni^{2+} and Co^{2+} do not interfere; Ca^{2+} does not interfere even if present in 300-fold excess.

Further work on the applicability of this method for the determination of Mn^{2+} in soils, plants, fruits, steel and fertilizers (micronutrients), etc. is in progress.

TABLE 1—CONCENTRATION DEPENDENCE (h_{max})

Sl. No.	Manganese, ppm	E_{max}, V	Height, div.	Sensitivity	Current, μA
1.	01.00	−1.6	08.00	1/2	00.040
2.	07.72	−1.6	13.00	1/2	00.065
3.	09.94	−1.6	19.00	1/3	00.143
4.	52.03	−1.6	48.00	1/2	00.240
5.	99.44	−1.6	21.00	1/10	00.525
6.	196.13	−1.6	32.00	1/10	00.800
7.	289.53	−1.6	32.00	1/15	01.200
8.	467.53	−1.6	41.00	1/20	02.075
9.	635.10	−1.6	39.00	1/30	02.925
10.	800.00	−1.6	28.00	1/50	03.560

from the said maxima (at —1.6) and Fe^{2+} and Fe^{3+} steps are very well separated, without chance of interfering with the estimation.

The plot of concentration of Mn^{2+} Vs. height of maxima (h_{max}.) gave a straight line (Fig. 2) which has been used as a calibration curve for the estimation of Mn^{2+} in calcite samples. Five samples from different horizons in India were analysed (Table 2). The results were in conformity with the results obtained by spectrographic, atomic absorption spectral and Electron pra-

TABLE 2—ANALYSIS OF MANGANESE IN DIFFERENT CALCITE

Sl. No.	Source	Colour	Manganese, ppm.
1.	Orissa	White	2914
2.	Bihar	Light green	1590
3.	Andhra Pradesh	Light blue	1190
4.	Andhra Pradesh	Light Yellow	0860
5.	Gujarat	Violet	0110

Acknowledgements

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Hydrogen sulphide absorption activity of hydrated iron oxide in the form of granules appears to depend on its moisture content. The rate of absorption generally falls with increasing moisture content of the oxide. In exceptional cases the mass retained its full activity even with 24.18 per cent free moisture under comparable operating conditions. With 14.8 to 16.7 per cent moisture in the oxide mass the treated gas was practically free of hydrogen sulphide at linear and space velocities of 900 m/hr and 250 v/v/hr respectively. When the mass is fully staurated with water its hydrogen sulphide removal efficiency dropped to 80-90 per cent of its original value.

Effect of Moisture on Hydrogen Sulphide Absorption Activity of Hydrated Iron Oxide

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The dry box purification process uses hydrated oxide of iron mixed with inert diluents or suitable supports for the removal of hydrogen sulphide from semi-water, coke oven and carbon dioxide gases. The process is the simplest one and is used widely even today. But the operation of the purifiers is not quite trouble-free. The operating conditions vary widely depending on design requirements. The operating pressure ranges between a few mm. of mercury/cm² to 18-20 kg/cm², while other variables such as gas throughout, linear velocity etc., also vary widely. Some typical conditions existing in commercial plants are reproduced below.

	Type I	II	III	IV
Operating pressure	15-17, kg/cm²	100-150 mm. of Hg	50-100 mm.of Hg	50-100 mm. of Hg.
H_2 in the inlet, ppm	200-1000	200-500	1500-2000	400-600
Total gas flow, M³/hr.	35000-45000	10000-11000	10000-11000	40000-50000
Space velocity, v/v/hr.	200-300	50-60	15-20	50-100
Linear velocity, m/hr.	300-400	800-1000	200-300	50-80
H_2S at the outlet, ppm	2	3	Traces	60-80
Feed gas	Converted semi-water gas	CO_2 gas	Coke oven gas	Semi-water gas

For efficient functioning, it is essential that the oxide should have a desirable moisture content. It appears that the upper and lower limits of the moisture content for proper functioning of the oxide may vary widely depending on the physical characteristics of the purifying mass. Experience indicates that the moisture content of the feed gas is a very important factor for controlling the moisture content of the oxide in the box. There are a number of factors which determine the moisture distribution in the mass along the direction of flow of the gas. For a highly active oxide, the major portion of the reaction of hydrogen sulphide with the oxide may take place in the box near the inlet, while with high hydrogen sulphide in the feed there may be appreciable temperature rise in the reaction zone. As a result, the gas temperature will rise and pick up some additional moisture from the bed. As the gas carrying higher moisture content travels in the down-flow direction, it cools down gradually and deposits its excess moisture in the bed at the cooler region. Thus, it is often found in commercial plants that the mass near the gas inlet dries up slowly but at the same time some condensate accumulates at the bottom which has to be occasionally drained out. If the feed gas is not saturated with water, the bed near the gas inlet side will almost certainly dry up at a faster rate causing hardening of the mass resulting in loss of activity, channelling and other associated difficulties. In most of the plants water or steam is sprayed in the gas before it enters the box.

The moisture content of the oxide has another important bearing with the regeneration of the oxide. A minimum amount of moisture in the oxide mass is essential for regeneration of the sulphide to oxide. A minimum moisture content is also essential for retaining the activity of the oxide.

In an earlier investigation[1] in this laboratory, it was observed that a moisture content of the oxide above 5 per cent does not have any significant influence on the rate of hydrogen sulphide absorption by hydrated oxide, and upto 30 per cent of the moisture content of the mass rate of hydrogen sulphide absorption remains unaffected. The above investigation was done with 1-2 g. of oxide blended with wood shavings and pure hydrogen sulphide as feed. The activity of the granulated purifying material unblended with fluffing material, however, appears to depend more intimately on the moisture content of the mass and with increasing moisture content activity of the mass falls and hydrogen sulphide slippage increases. In the present investigation, attempts were made to study the influence of moisture content in gas purifying mass on their absorption rate. The operating variables were maintained so as to simulate prevailing commercial practice. But the studies were conducted only at atmospheric pressure. The performance of the oxide mass was also studied in pilot plant scale using 15-20 l. of purifying material.

Experimental

Five varieties of oxide were selected for the study. Three of these have commercial application and two were prepared on laboratory scale. The materials were sized to 2-5 mm granules and sprayed with water. Initially the moisture content of the mass was kept higher than required and then dried to bring down the moisture content to the desired level. In bench scale investigation, the mass was charged in M.S. reactors of 25-40 mm i.d. Semi-water gas of the following composition was used as feed gas: Carbon dioxide 8-10 per cent, carbon monoxide 28-32 per cent, hydrogen 35-38 per cent and rest nitrogen. The feed gas was first made free from hydrogen sulphide and then calculated amount of the latter introduced in the stream. All the experiments were conducted at room temperature. For pilot plant investigation, a feed gas containing 82-85 per cent carbon dioxide and rest hydrogen was taken.

Results and Discussion

1. *First Stage*: The results of the bench scale experiments are presented in Table 1. The iron contents of the mass vary from 33.3 to 56.70 per cent as ferric oxide. All the three varieties of oxide have commercial use. It has been found by a separate Nesbitt test that all the iron oxides present in the samples are active for absorption of hydrogen sulphide. In these experiments hydrogen sulphide in the feed gas has been kept constant at 400 ppm. Moisture has been varied from 9.42 to 24.18 per cent. The effect of linear and space velocities has been studied upto 360 m/hr and 706 v/v/hr (maximum) respectively and not separately. The result may be interpreted taking either the linear or space velocity as reference, pH of the mass (10 per cent suspension in water) of the different samples was between 7.6-8.0.

It might be observed that the rate of hydrogen sulphide absorption falls in general with increasing gas throughput irrespective of the previous history of the purifying mass. But the higher ferric oxide seems to have a positive advantage over the mass having lower ferric oxide content. The performance of samples S_2 and S_3 cannot be compared on the same basis. Here leakage of hydrogen sulphide with S_3 is much less than that in case of S_2 though their iron oxide content is almost same.

The effect of moisture on activity is quite interesting.

TABLE 1—ACTIVITY OF HYDRATED IRON OXIDE WITH INCREASING MOISTURE CONTENT

[H_2S in the Feed = 400 ppm]

Sample	Moisture, %	Iron as Fe_2O_3 (on dry basis), %	Linear Velocity, m/hr.	Space Velocity, v/v/hr.	H_2S Concentration, v/v ppm.
S_1	12.1	35.45	10)	196	Exit not traceable
			150	294	1
			200	392	1
			360	706	3
	21.70	—	260	350	28
	24.32	—	200	392	32
S_2	9.42	55.80	200	392	1
			360	706	1
	23.44	—	200	392	3
			360	706	11
S_3	20.53	54.10	200	392	1
			360	706	1
	24.18	—	200	392	1
			360	706	1

For comparing the performance at various moisture contents the data at higher space velocities only have been taken into consideration. In case of S_1 with higher moisture content, experiments were conducted at space velocities of 350 and 392 only, because even at this velocity leakage of hydrogen sulphade was considerable. In case of S_1 with 12.1 per cent free moisture hydrogen sulphide leakages are 1 and 3 ppm at space velocity 392 and 706 respectively. At 21.7 and 24.32 per cent moisture, hydrogen sulphade leakage shoots upto 28 and 32 ppm respectively.

In case of S_2 with 55.8 per cent ferric oxide, leakage of hydrogen sulphide with the same gas throughput is less, but hydrogen sulphide removal rate falls with increasing moisture content of the mass. At 9.42 per cent moisture the performance of the mass is quite satisfactory and hydrogen sulphide in the purified gas is less than 1 ppm. When the moisture content is raised to 23-24 per cent 11 ppm of hydrogen sulphide slipped at space velocity 706. The performance of the S_3 appears to be least affected by moisture content upto 24.18 per cent. The results at lower moisture content for this sample has not been included in the table because in the product gas hydrogen sulphide could not be detected under the experimental conditions.

It may be concluded that free moisture has a definite influence on the activity of the mass. But moisture tolerances with respect to activity are not the same for oxides from different sources. Moignard[2,3] recommends supported iron oxide of open texture and 30-50 per cent moisture consistent with unrestricted gas flow for proper functioning of the oxide. The observation in the present investigation differs with the above findings; may be at higher moisture content the physical parameters play vital role in determining the activity of the mass.

2. *Second Stage*: In the second stage the problem was studied further in large scale units. Two reactor tubes of 3″ diam, and 6′ long were installed. These were connected in series and carbon dioxide-enriched gas (85 per cent CO_2) was taken as feed. Hydrogen sulphide concentration in the feed varied between 41 and 838 ppm. Two batches of oxide of 10 mm. diam. extrudates were charged. The experiments were conducted for 190 and 200 hr. respectively. In all the tests space and linear velocities were fixed at 250 v/v/hr. and 900 m/hr respectively. The gas was saturated with water vapour at the ambient temperature before it entered the oxide bed.

Investigations were conducted in two steps. In the first about 15-16 per cent of free moisture was added to the mass and then the activity noted. It is known that condensation of water takes place in the box in commercial plants and under such condition moisture

accumulates in the oxide to its maximum retention capacity. To study the behaviour of the oxide at its maximum moisture retention capacity the oxide mass was completely soaked with water and then its absorption activity studied (Table 2).

It may be observed that the activity of both the samples S_4 and S_5 containing 77.84 and 80.0 per cent iron as ferric oxide respectively is remarkably high when they contain 15-16 per cent free moisture in the mass. The unit with S_4 was operated for 190 hr continuously with lower moisture content and 855 M^3 gas passed. With hydrogen sulphide concentration varying from 372 to 838, it has removed completely hydrogen sulphide in all stages. The moisture content of the S_5 was 14.8 per cent and hydrogen sulphide concentration varied from 17 to 763. Here too treated gas was always free of hydrogen sulphide.

There was marked difference when the oxides were fully soaked with water. The oxide mass appears to have completely lost its activity after it was fully soaked in water when hydrogen sulphide measured at the inlet and exit, was found the same. But the oxides regained their activity after some time with passage of gas but not the original activity. S_4, when fully soaked in water, can remove more than 90 per cent hydrogen sulphide and leakage varied from 12 to 255 ppm hydrogen sulphide depending on the inlet concentration. The activity of S_5 appears to be more adversely affected. In this case the activity dropped by about 20 per cent when the mass is fully saturated with moisture. In an earlier investigation, It was observed that an oxide mass with 35 per cent moisture would completely absorb hydrogen sulphide from carbon dioxide at a comparatively lower gas throughput and linear velocity[4]. In the present investigation space and

TABLE 2—Pilot Plant Test Results

[Linear and Space Velocities were kept Constant at 900 m/hr. and 250 v/v/hr. respectively]

Sample	Moisture, %		Concentration of H_2S, ppm		Hours of Run (cumulative)	Cumulative gas flow, M^3
			Inlet	Outlet		
S—4	16.65		372	Nil	—	—
	16.65		480	,,	—	—
	16.65		523	,,	—	—
	16.65		610	,,	190	855
	16.65		654	,,	—	—
	16.65		763	,,	—	—
	16.65		838	,,	—	—
	Tube I	Tube II				
	37.0	38.0	42	42	192	864
	32.0	37.5	765	255	208	936
	29.9	37.5	229	12	224	1008
	26.6	37.6	357	19	245	1102.5
	25.2	37.4	485	50	264	1208
	25.7	36.3	434	25	274	1233
S—5	14.8		109	Nil	200	900
	14.8		532	,,	—	—
	14.8		763	,,	—	—
	14.8		77	,,	—	—
	14.8		552	,,	—	—
	37.4	38.3	280	276	202	909
	36.2	37.6	255	51	224	1080
	35.5	36.98	485	76	246	1107
	34.7	37.2	434	32	218	1206

linear velocities were high and the oxide mass was not blended with any fluffing material as was done earlier. The difference in physical character of the mass may be responsible for their unlike performance.

Another interesting feature is the changing moisture content of the oxides during operation. In case of S_4, free moisture content of the mass in the first tube gradually dropped from 37 and seems to have stabilized at 25 per cent. The moisture content of the second tube remained practically steady. In the case of S_5, free moisture content of the first tube dropped a little but second tube was not affected at all. The fall of moisture content may be explained by assuming that due to the reaction at the top, temperature of the gas rises and it picks up some moisture from the reaction zone at the top and carry it to the down-flow region. Drying up in the top will be faster when the oxide is more active and the concentration of hydrogen sulphide in the feed is high. This is not an uncommon feature in the commercial plant that mass is drying up at the entry side but at the same time condensate is accumulating at the bottom. It appears that the maximum water retention capacity of the oxide mass may have a relation with its efficient performance in an industrial unit. By reversing the flow, this situation can be controlled. Further investigation on this line is under progress.

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Storage behaviour of a mixture of granular triple superphosphate and prilled urea has been studied. A rapid deterioration in the product is observed even when the mixture is stored in stoppered bottles. The presence of free phosphoric acid in TSP is found to delay, to some extent, the deterioration of the blended fertilizer. Hygroscopicity of TSP with varying ratios of H_3PO_4/H_2O has been determined.

Blending of Urea Prills with Granular Triple Superposphate

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The term 'bulk blending', now widely in use, consists essentially of mixing granular fertilizers to make multinutrient formulations. The keeping quality of the granular blends is superior to that of pulverized mixtures. While most of the fertilizers are compatible, a few of these create difficulty when blended. For instance, a blend of urea with normal or triple superphosphate (TSP) tends to lose its free-flowing characteristics rather rapidly and becomes wet and sticky. This deterioration has been attributed to the formation of urea-monocalcium phosphate (MCP) adduct and consequent release of water of crystallization, according to the following equation:

$$4\,CO(NH_2)_2 + Ca(H_2PO_4)_2.H_2O = Ca(H_2PO_4)_2.4CO(NH_2)_2 + H_2O$$

The released water forms saturated solution of soluble constituents, thereby generating enough liquid phase to cause stickiness and loss of free-flowing characteristics[1,2].

Though these facts are now well established, no

studies are reported in the literature on the extent of deterioration of urea-TSP blends with passage of time. In continuation of our previous communication[3], in which studies were made on the problems involved when urea is granulated with TSP, the present work relates to the study of the effect of blending prilled urea with granular TSP with similar particle size distribution.

Experimental

Fertilizer grade urea prills of $-10+16$ mesh (B.S.S.) size were used in the present series of experiments. Fully cured granular TSP (imported) with negligible amount of free phosphoric acid and of a similar size distribution as that of urea was used for blending.

Free phosphoric acid in TSP was adjusted in various samples by adding the required amount of phosphoric acid (conc.) and drying the granules to obtain products of the desired free phosphoric acid concentration. Moisture in both urea and TSP were adjusted by exposing the samples to 100 per cent relative humidity.

Bulk blends prepared were incubated at room temperature. Physical condition of all the blends was noted after predetermined intervals of time. Hygroscopic behaviour of some of the samples were studied by subjecting them under stagnant condition to an atmosphere of 81 per cent relative humidity and the increase in weight on account of moisture absorption recorded.

Results and Discussion

To disentangle the deterioration on account of the hygroscopic nature of the blended product and the deterioration on account of adduct formation, the samples were kept in corked bottles. It was found that there was a steady deterioration of the blended product with passage of time.

The first step appears to consist of urea prills forming an agglomerate with a TSP granule as a nucleus. The agglomerate increases in size, at the same time the product appeared increasingly moist. Finally, a stage is reached when the whole blended product forms a pasty mass.

It is difficult to describe the slow and gradual change taking place in the blended product. However, for convenience the process of deterioration may be characterized as follows:

Stage 1—In this stage the blended product appeared dry and on tilting the bottle the free-flowing characteristics of each granule were observed.

Stage 2—Few agglomerates appear, the bulk was free-flowing. But slight moistness observed.

Stage 3—The agglomerates increase in size and multiply. Moistness increases and free-flowing characteristics are distinctly affected.

Stage 4—Completely moist and pasty without any free-flowing characteristics.

The results are presented in Table 1. The samples of the blended product with varying moisture and free phosphoric acid are incubated at room temperature and

TABLE 1

Sample No.	Constituents of the Blend	Initial Moisture, %	Free Phosphoric Acid as P_2O_5, %	The Day the Stage is Reached		
				Stage II	Stage III	Stage IV
S_1	Urea	0.1	—	6th day	10th day	18th day
	TSP	0.1	Nil			
S_2	Urea	0.5	—	3rd ,,	4th ,,	6th ,,
	TSP	1	3			
S_3	Urea	0.5	—	1st ,,	2nd ,,	3rd ,,
	TSP	2.5	Nil			
S_4	Urea	0.5	—	4th ,,	5th ,,	7th ,,
	TSP	0.1	3			
S_5	Urea	0.1	—	6th ,,	10th ,,	15th ,,
	TSP	0.5	1			
S_6	Urea	0.3	—	1st ,,	3rd ,,	6th ,,
	TSP	1.0	Nil			
S_7	Urea	0.3	—	3rd ,,	6th ,,	10th ,,
	TSP	1.0	3			
S_8	Urea	0.3	—	—	1st ,,	2nd ,,
	TSP	4.0	3			

the number of days taken to reach the various stages described earlier are recorded.

From the results, it is clear that when urea containing 0.1 per cent moisture is blended with granulated TSP containing no free phosphoric acid and very small amount of moisture, the deterioration is apparent only after the 6th day (2nd stage) and the product becomes completely moist and sticky after the 18th day (4th stage) of blending. On the other hand, when urea contained the same moisture but TSP with 1 per cent moisture and without any free phosphoric acid, the blended product shows deterioration after one day (24 hr.) (2nd stage) and the product becomes completely moist and sticky (4th stage) on the 6th day. This is understandable as moisture is considered necessary for adduct formation. Though even traces of solution of urea or MCP coming in contact with solid phase of either is sufficient to initiate the adduct formation nevertheless the rate of deterioration is slow as found in the present case.

The presence of free phosphoric acid in TSP is found to delay the deterioration of urea-TSP blends. The deterioration in the sample S_7 containing TSP with 1 per cent moisture and 3 per cent free phosphoric acid is detectable only after the third day and the blended product reaches the fourth stage on the 10th day. Whereas sample S_6 which contains urea and TSP with the same moisture content but without any free phosphoric acid starts deteriorating after the first day and the product becomes completely moist and pasty (4th stage) after six days.

A plausible explanation of such a behaviour appears to be due to the fact that the moisture absorbed by hard, smooth and relatively non-porous urea prills from the adjecent TSP granules resides mainly on the surface of the prills in the form of a saturated solution and is readily available for the adduct formation. This transfer of moisture from TSP granules to urea prills occurs on account of greater hygroscopicity of urea in comparison to TSP with low content of free phosphoric acid.

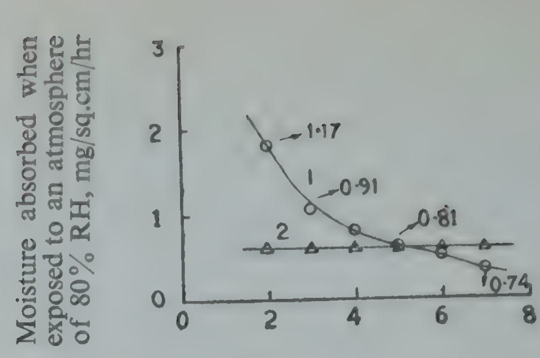

Fig. 1—Absorption of Moisture by Fertilizers
1. TSP with 3 per cent Phosphoric Acid
2. Urea

The situation, however, is changed when TSP contains a higher proportion of free phosphoric acid with high H_3PO_4/H_2O ratio. In this case, hygroscopicity of TSP is more than that of urea which in due course of time becomes comparable to that of urea and there is little transfer of moisture from TSP to urea and the surface of urea prills remains relatively dry. Some transfer of moisture may, however, occur on account of direct contact between the adjacent granules.

TSP granules are known to retain their free-flowing characteristics even when their moisture content is high. This is partly due to the nature of the granules as well as due to the fact that the less soluble MCP generates less liquid phase. Thus, the distribution of this liquid phase in TSP granules is such that only a small proportion is available on the surface for adduct formation. Consequently, the blended product remains free-flowing for a relatively longer time.

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The earlier concept of compatibility of fertilizers for the preparation of blends needs reappraisal when granular components are blended, as this involves minimum intergranular contacts. Keeping this in view, single superphosphate and calcium ammonium nitrate in granular form have been blended together and their behaviour studied especially with reference to the water solubility of the phosphatic component. Blends have been found to maintain the water-solubility of the phosphatic component for a considerable period of time.

Superphosphate and Calcium Ammonium Nitrate Granular Blends

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It is estimated that during 1969, 85 per cent of the total nitrogen and 52 per cent of the total P_2O_5 produced in this country consisted of straight nitrogenous and phosphatic fertilizers[1]. In order to meet the nutrient deficiencies, it is more convenient for the farmer to apply the needed nutrients in a single application rather than in split applications involving straight fertilizers. Blending of straight nitrogenous and phosphatic fertilizers to produce N:P formulations is one of the convenient means by which the requirements of these nutrients by the crop are met.

Calcium ammonium nitrate is considered incompatible with superphosphate[2] because the calcium carbonate of the CAN reacts with free phosphoric acid as well as aqueous monocalcium phosphate—the only water-soluble component of the superphosphates. This reaction leads to the reversion of the water-soluble phosphate into water-insoluble form. The blended fertilizer thus loses a part of its effectiveness on account of the loss of the water-soluble phosphate content of the fertilizer.

It has been demonstrated by various workers[3–8] that when monocalcium phosphate is mixed with limestone or calcium carbonate, under normal temperature conditions, it leads mainly to the formation of a water-insoluble but citrate-soluble dicalcium phosphate with a smaller portion of citrate-insoluble phosphate. It has been further stated that at higher temperature the phosphatic component gets reverted to the citrate-insoluble P_2O_5. This was confirmed by Bardhan *et al*[9], who granulated superphosphate and calcium ammonium nitrate by wetting, granulation and drying at 60°C under reduced pressure and found that water-soluble phosphate gets reverted to citrate-soluble and citrate-insoluble phosphate during processing and storage.

The compatibility/incompatibility of the various fertilizers, as indicated in the well-known diagram by Jacob and Uexkull[2] to serve as a guide for mixing fertilizers, is largely based on the studies with powdered mixtures, which were then widely prevalent. In recent years, there has been a spectacular growth of bulk blending in the USA in which the components mixed are in the granular form. Granular blends possess better uniformity and have superior free-flowing characteristics than the powdered mixtures. Intergranular contact in the granular blends are greately minimized and any possible adverse reaction between the components may be less significant. In view of this, the whole concept of compatibility needs reappraisal when granular fertilizers are mixed or blended.

Although most of the superphosphates produced in this country are in the powdered from, there are indications that some of the manufacturers are intending to produce granular superphosphate. This is a welcome development, which may, in future, lead to the adoption of granular blends as a means to supply balanced fertilzers in preference to powdered mixtures presently in use. It should, however, be borne in mind that the particle size distribution of granular superphosphate should match with the nitrogenous component with which it is to be blended. This is important because it

has been shown that segregation in the blended fertilizers after mixing is minimized when the particle sizes of the components are alike[10].

In this communication studies have been made with the granular blends consisting of CAN and single superphosphate. The extent of reversion of water-soluble phosphate has been estimated at various intervals of time.

Experimental

Powdered superphosphate (total P_2O_5 19.72 per cent, water-soluble P_2O_5 16.98 per cent and citrate-insoluble P_2O_5 0.25 per cent) was granulated in a paddle-type granulator without using any granulation aid. Good granules were obtained only when large proportion of water was initially added and the slurry thickened to a paste. The processing temperature during granulation was varied from 60 to 100°C. The analysis of granular superphosphate on dry basis is as follows: Total P_2O_5 19.76 per cent, water-soluble P_2O_5 16.82 per cent and citrate-insoluble P_2O_5 0.26 per cent.

For better understanding of the problem of reversion, it was thought necessary to include a sample of superphosphate, which was cured and contained minimum of free phosphoric acid. CAN used in the experiments was obtained from Nangal factory of the FCI Ltd.

Before mixing, both the components, viz. single superphosphate and CAN, were dried to constant weights over sulphuric acid (conc.) and then the required amount of moisture introduced by exposing the sample to 100 per cent relative humidity. The fertilizers were individually kept for a day or two so that the moisture gets evenly distributed in the granules. The two components were then blended to a ratio of 2-1-0 and placed in air-tight bottles and incubated at room temperature (~30°C). About 1 g. samples of single superphosphate were withdrawn at various intervals of time and analysed.

Results and Discussion

A study of the pulverized CAN and superphosphate has been reported by Kanwar *et al*[11]. They found that the blended superphosphate lost its water-solubility at a rapid rate—the water-solubility of the 1-1-0 product was reduced to 35.7 per cent of the original in 24 hr., The results of the present work are given in Table 1, which indicate that the loss of water-solubility in the case of granular blended product is extremely slow, viz. it takes 4-5 months for about 50 per cent decrease in water-solubility. This is so because of the reduced area of contact between the particles and also due to the fact that the larger proportion of the moisture present in the form of saturated solution of ammonium nitrate and monocalcium phosphate reside inside the respective granules.

There is a slight increase in the reversion of the water-soluble P_2O_5 when the particle sizes of the nitrogenous and phosphatic components are different. In this case, the area of contact between the granules is likely to be more. The effect of increase of moisture in the blended product (Table 1) is found to increase the extent of reversion.

TABLE 1—PERCENTAGE REVERSION OF WATER-SOLUBLE PHOSPHATE IN 2-1-0 BLEND CONTAINING GRANULAR CAN AND GRANULAR SINGLE SUPERPHOSPHATE

	Moisture Contents of the Blend		Time, days							
	CAN	SSP	1	15	30	60	90	120	150	180
A	(−5+8) 2%	(−5+8) 4%	3.62	10.05	10.82	13.67	19.20	33.88	42.26	48.57
B	(−5+8) 2%	(−5+8) 8%	4.51	16.47	18.31	21.04	24.73	37.57	48.57	52.25
C	(−5+8) 2%	(−8+10) 4%	3.62	9.09	10.94	19.20	26.10	48.57	52.25	55.94
D	(+5) 2%	(−5+8) 4%	3.62	10.05	15.52	28.42	38.52	44.94	52.25	54.99

Citrate-insoluble phosphate in each case was found to be less than 0.5%

When CAN and single superphosphate are blended, the first step is the reaction between the calcium carbonate of the CAN and free phosphoric acid invariably present in superphosphates. This is a relatively fast reaction leading to the reversion of water-soluble P_2O_5. Another reaction, which is slow and causes the reversion of the water-soluble component in a gradual manner during storage, is probably initiated by the hydrolytic decomposition of monocalcium phosphate leading to the formation of phosphoric acid, which then reacts with calcium carbonate as represented by the following overall equations:

$$Ca(H_2PO_4) \rightleftharpoons CaHPO_4 + H_3PO_4$$
$$2CaCO_3 + 3H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + CaHPO_4 + 2H_2O + 2CO_2$$

The fact that the slow reversion is initiated by the phosphoric acid formed by the hydrolytic decomposition of monocalcium phosphate is supported by the experimental evidence given by Larsen *et al*[8], who passed air saturated with water vapour in a column containing monocalcium phosphate layer placed over that of calcium carbonate. X-ray diffraction analysis of the cake formed at the top of the calcium carbonate layer was found to consist mainly of dicalcium phosphate dihydrate.

The extent of reversion of the water-soluble P_2O_5 arising on account of the reaction between calcium carbonate and free phosphoric acid present in superphosphate is of considerable importance as this reaction is relatively fast and is likely to be completed during the time that elapses when the components are blended and finally applied to the soil. Therefore, it is advisable to use cured superphosphate containing minimum of free phosphoric acid for blending purposes in order to minimize the reversion of the water-soluble component of the superphosphate.

Acknowledgement

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Experimental investigation on the reduction of gypsum by carbonaceous fuels has been carried out in the laboratory. The various factors, like ratio of the gypsum to coal, coke breeze and lignite, also temperature and period of heating on the conversion of gypsum have been studied. The optimum conditions for the conversion of calcium sulphate in gypsum to calcium sulphide were found to be (a) gypsum/coal ratio as 2: 1, (b) temperature 900-950°C and (c) period of heating 45 to 60 minutes.

Sulphur from Gypsum: Reduction of Gypsum to Calcium Sulphide

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Introduction

India is faced with acute shortage of sulphur. Furthermore, the elemental sulphur requirements are rapidly increasing in line with the plan targets established for sulphur consuming industries, highest priority being accorded to the fertilizer industry. Gypsum occurs fairly extensively in the country[2], but the known deposits are either low grade or uneconomic to exploit. A variety of processes have been developed to recover sulphur from low grade[3–9] gypsum including one based on the reduction of gypsum to calcium sulphide, liberation of hydrogen sulphide from the calcium sulphide[10–12] and production of sulphur from hydrogen sulphide by the conventional Claus process. The present investigation was carried out to determine the extent of the reduction of gypsum by coal, coke and lignite. Such a study will obviously be very useful in the development of commercial process.

Experimental

Natural gypsum from Rajasthan was used for this study. Reducing agents used were coal, lignite and coke breeze. Gypsum and the reductants were powdered to pass through 150 mesh (B.S.S.). The materials were mixed in various proportions and the mixed sample heated in a silica crucible closely covered with a silica lid in an electrical muffle furnace maintained at the required temperature. After a specified period, the crucible was taken out and cooled. The sulphide-sulphur in the reduced sample was estimated by liberation of hydrogen sulphide with acid and absorbing it in cadmium acetate solution, the cadmium sulphide being estimated iodometrically. From the weight of gypsum taken for reduction, the weight of the reduced sample and hydrogen sulphide content in the reduced sample the conversion of sulphate to sulphide were calculated.

Results

Analysis of gypsum and proximate analyses of coal, coke breeze and lignite used for the study are given in Table 1. Gypsum and coal have been mixed in different proportions and the reduction studied at 900°C for 1 hour. The results are given in Table 2. Gypsum and coal powder (ratio 2:1) were mixed with different proportions of water. The effect of temperature and time on the reduction was studied at 800, 850, 900 and 950°C. For this, gypsum was mixed with different reducing agents, like coal, coke or lignite. The results are shown in Fig. 1. Each value in the plotting was obtained from a separate experiment.

Discussion

The optimum proportion of gypsum to coal required for almost quantitative reduction of calcium sulphate to calcium sulphide was found to be 2:1 by weight (Table 2). This works out to calcium sulphate-fixed carbon as 1:4 by molar ratio. The same optimum weight ratios were followed in the case of coke breeze and lignite (partially dried); the mole ratio of calcium sulphate and fixed carbon in these cases being 1:5.8 and 1:3.3 respectively. The mole ratio of calcium sulphate and total carbon in

TABLE 1—ANALYSES OF THE RAW MATERIALS

Gypsum		Reductant			
Constituents	Weight, %	Constituents, %	Coal	Lignite (partially dried)	Coke Breeze
CO_2	0.2	Moisture	1.2	10.6	0.8
		Ash	15.0	10.8	24.1
Combined Moisture	18.8	V.M.	34.2	36.6	1.6
		F.C.	49.6	42.0	73.5
CaO	29.1				
MgO	0.3				
SO_3	41.6				
SiO_2	6.3				
Al_2O_3	2.3				
Fe_2O_3	1.4				
$CaSO_4, 2H_2O$	89.5				

all these cases were also calculated. This works out to 1:5.64, 1: 5.6 and 1: 4.34 in the cases of coke breeze, coal and lignite (partially-dried) respectively. This shows that on the basis of carbon utilization and efficiency of reduction lignite is superior to coal, the worst being coke breeze.

The effect of temperature and time for the reduction (Fig. 1) shows that temperature is the intensive factor for the reductive reaction. Below 900°C, the reaction is slow while at 950°C it is quite fast. In the case of coal at 900 to 950°C, almost 95 per cent of reduction is achieved in 1 hour. In the case of lignite maximum reduction was achieved after 45 min. at both 900 and 950°C. This period probably could be further reduced by use of a rotary kiln or a fluidized bed reactor due to better and uniform heat distribution for which further studies are in progress. After the reduction is almost complete, further continuation of heating indicates a lowering of the conversion probably due to oxidation of the sulphide due to leakage of air and absence of carbon to provide a reducing atmosphere. It was also observed that in the batch process of reduction presence of a slight trace of carbonaceous material in the reduced gypsum is necessary to be sure for a reducing atmosphere, otherwise a small part of reduced calcium sulphide is likely to be oxidized. Reduction of gypsum with coke breeze was observed to be quite slow even at 950°C as only 71 per cent could be reduced even in 1½ hours, (Fig. 1).

TABLE 2—EFFECT OF GYPSUM/COAL RATIO ON THE REDUCTION OF GYPSUM

(Reduction Temp. 900°C; Reduction time 1 hr.)

Gypsum: Coal (by weight)	$CaSO_4$: Fixed Carbon (mole ratio)	$CaSO_4$: Total Carbon (mole ratio)	Reduction of $CaSO_4$ in Gypsum, %
60:40	1:5.3	1:7.5	88.9
67:33	1:4.0	1:5.6	93.0
70:30	1:3.4	1:4.8	81.1
75:25	1:2.6	1:3.7	66.4

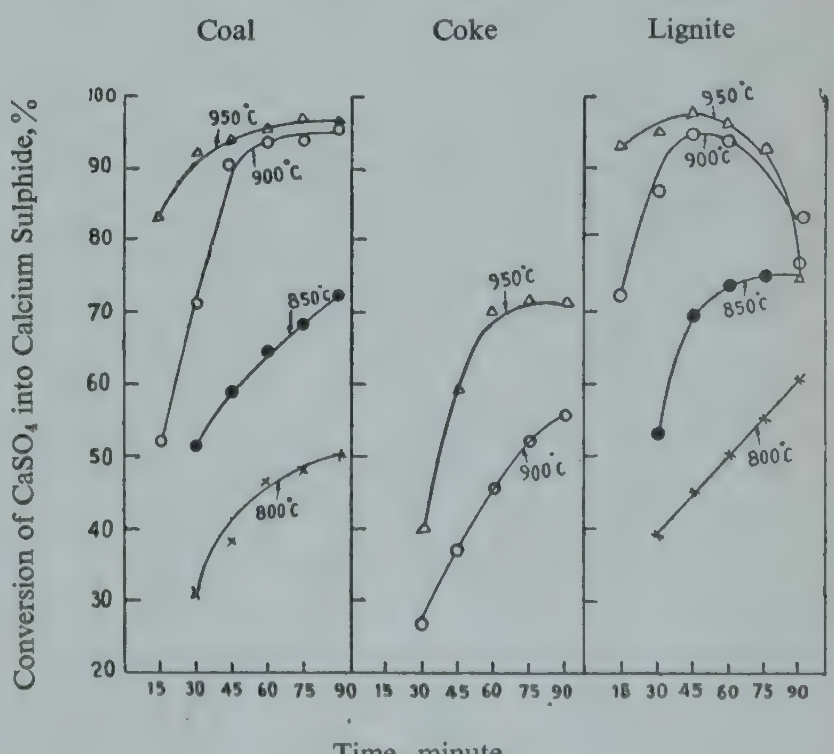

Fig. 1—Effect of Temperature and Time on Reduction

Conclusion

Gypsum could be reduced to calcium sulphide almost quantitatively using coal in the ratio of gypsum/coal as 2:1. The other reducing agents, viz. coke breeze or lignite, could also be used for reduction. Although dry lignite is more effective than coal or coke breeze in reduction, this would necessitate drying of raw lignite which contains a high quantity of moisture. The reaction rate is quite appreciable at 900°C and sufficiently fast above it. Above 950°C gypsum begins to decompose with the simultaneous production of lime and sulphur dioxide. For reduction with a reasonable degree of conversion and with the minimum formation of sulphur dioxide, a temperature of 900 to 950°C seems to be optimum. Experiments in the laboratory indicate that the time for reduction may vary from 45 min. to 1 hour.

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Infrared spectrophotometric and thermogravimetric studies on epoxide resins, developed in this laboratory, were carried out. The resins included liquid to solid types of different epoxide equivalents and other characteristics. The above characteristics of different epoxide resins marketed under various trade names are given for comparison.

Epoxide Resins—Their Infrared Spectrophotometric And Thermogravimetric Studies

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The communication deals with the study of epoxide resins by infrared spectrophotometry and thermogravimetry to give further support and confirmation to the previous results[1] as well as the method of preparation.

Infrared Spectrophotometry

This technique has been used for elucidating the structural characteristics of epoxide resins. The epoxy and other groups determine the functionality and cross-

linking density, which in turn establish the rigidity, thermal stability and solvent resistance of the cured product by the use of a suitable curing agent. The structure also determines an important property, viz. viscosity.

A Perkin-Elmer infrared grating spectrograph (model 421) having wave length ranging from 2.5 to 18 micron was used, and the records for all the samples were taken with identical parameter adjustment; the time taken for recording the full range was about 17 min.

The spectra of liquid resins were recorded by taking a small drop in between two potassium bromide crystal windows, which were pressed to have the desired path length. For the solid resins potassium bromide pellets were employed. About 3 mg. of finely powdered resin were mixed with 300 mg. of dry potassium bromide powder (pre-dried at 400°C) and the mixture was pressed in a die under a vacuum at 20 tons. The tablet thus made, was 13 mm. in diam. and nearly 0.8 mm. in thickness.

Infrared spectra of various resins of different physical states, epoxide equivalent and molecular weights are given in Tables 1 and 2. Their corresponding spectra are shown in Figs. 1 & 2.

Epoxide resins A to G were prepared from bisphenol —A and epichlorohydrin in this laboratory. The important peaks (Figs. 1 & 2) of these resins are of epoxy, substituted aromatics, hydroxy, ether, methyl and methylene groups. Identical peaks were also found in almost all commercial resins under observation, thus establishing purely diglycidyl ether of bisphenol A (Figs. 1 & 2). Further peaks except those of epoxy, are in the increasing order from viscous to more viscous liquids/solids. This increasing tendency is explained on the basis of increase in 'n' value as shown by general formula given below:

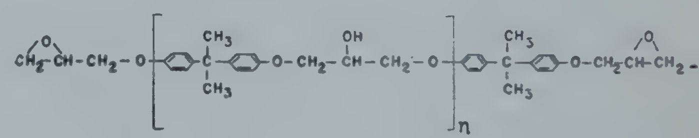


TABLE 1

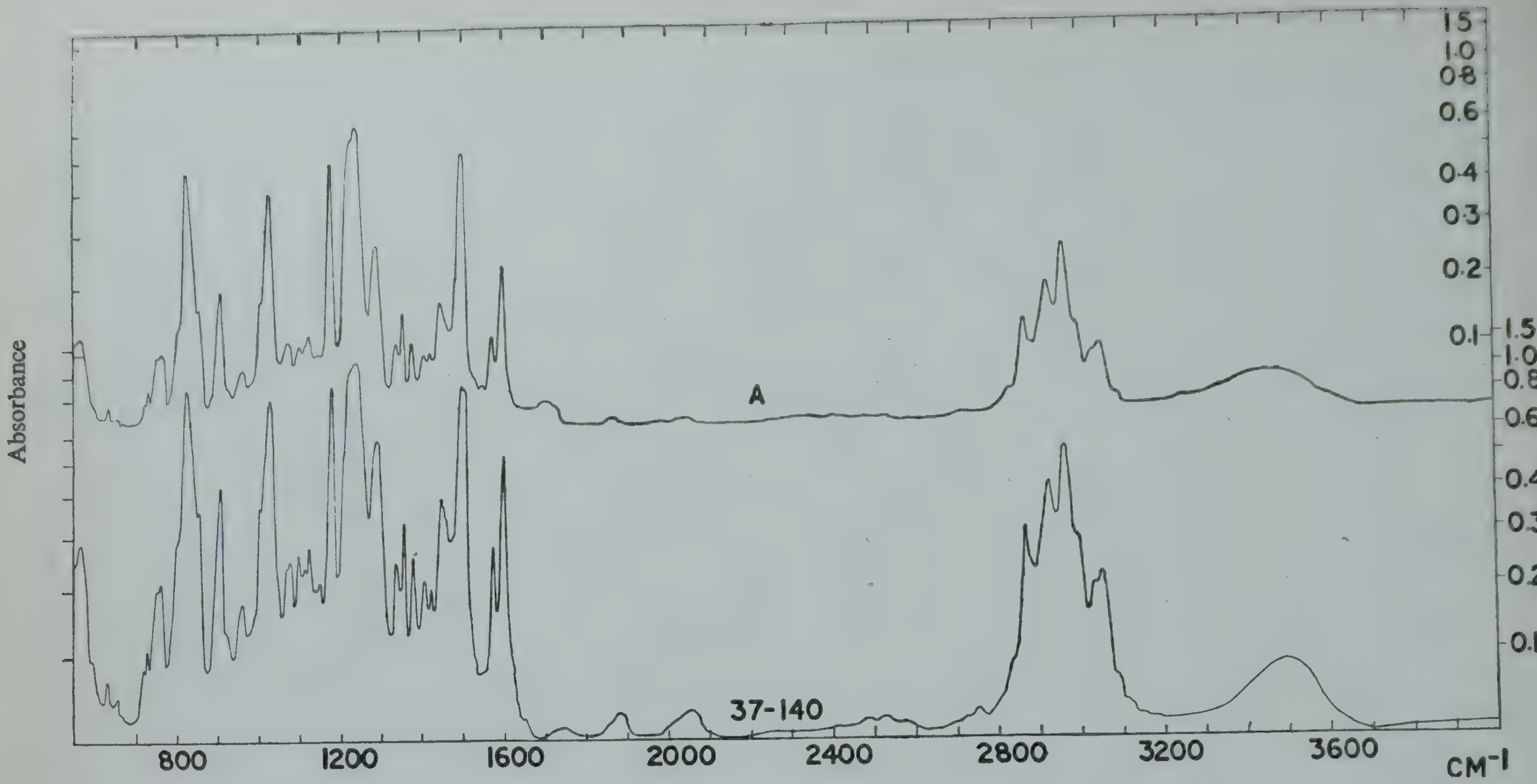
Sl. No.	Resins Prepared in the Laboratory	State	Commercial Resins & Their Number
1.	A	Liquid	37-140*
2.	C and D	Solid	37-301* and 1001†
3.	F	Solid	37-304* and 1004†
4.	G	Solid	1007†

* Epotuf Resin; Reichhold Corpn. U.S.A.
† Epon Resin; Shell Chemical Co., U.S.A.

TABLE 2—CHARACTERISTICS OF DIFFERENT RESINS

Sl. No.	Manufacturer and Trade Name	Resin No.	Epoxide Equivalent*	Molecular Weight†	Melting/Softening Point, °C
1.	Prepared in this laboratory	A	216	316	10-20
		C	600	825	55-59
		D	593	930	58-61
		F	875	1700	80-90
		G	1000	1550	78-90
2.	Reichhold 'Epotuf'	37-140	185-200	—	—
		37-301	450-525	—	60-68
		37-304	875-1000	—	93-104
3.	Shell Chemical Co., 'Epon'	1001	450-550	900-1000	65-75
		1004	800-1025	1400	95-105
		1007	2000-2500	2900	125-135

*Determined by Pyridinium chloride method.
†Determined by Osmometer.
For items 2 and 3, values have been taken from *Handbook of Epoxy Resins* by Henry Lee and Kris Neville (McGraw Hill Book Co. Inc., New York), 1967.



Frequency, cm^{-1}

Fig. 1—Infrared Spectra of Liquid Epoxy Resins

In the earlier communication[1], epoxide resins prepared in this laboratory were compared with those of commercial resins on the basis of epoxide equivalent, molecular weight etc. A similar grouping pattern was followed in presenting different figures (Figs. 1 & 2). However, resin 'G' (Ep. Eq. = 1000; Mol. wt. = 1550), which was compared earlier with Epon '1004' (Ep.Eq. =800−1025; mol. wt. = 1400), is also comparable with Epon '1007' (Ep.Eq. = 2000-2500; mol. wt. 2900); others are comparable infrared spectro-photometrically (Figs. 1 & 2).

Thermogravimetry

Thermogravimetric analysis has been carried out in a Stanton thermogravimetric balance (Model HTD), having 350°C/hr rise in temperature. The number of thermograms were taken for weighed (0.09 g.) samples of solid and liquid resins (Figs. 3-6). The details and observations from the above figures are tabulated below (Table 3).

TABLE 3

Sl. No.	Resin	Fig. No.	Rapid Loss at Temp., °C		Time Taken from 'd' to 'e', min.	Starting Weight of Sample, g.	Total Weight-Loss from Figs., g.
			Started	Completed			
(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
1.	G (solid)	3	390	615	40	0.09	0.0897
2.	Epon 1001 (solid)	4	400	600	40	0.09	0.0894
3.	A (liq.)	5	350	640	55	0.09	0.0899
4.	Epotuf 37-140 (liq.)	6	330	620	50	0.092	0.0918

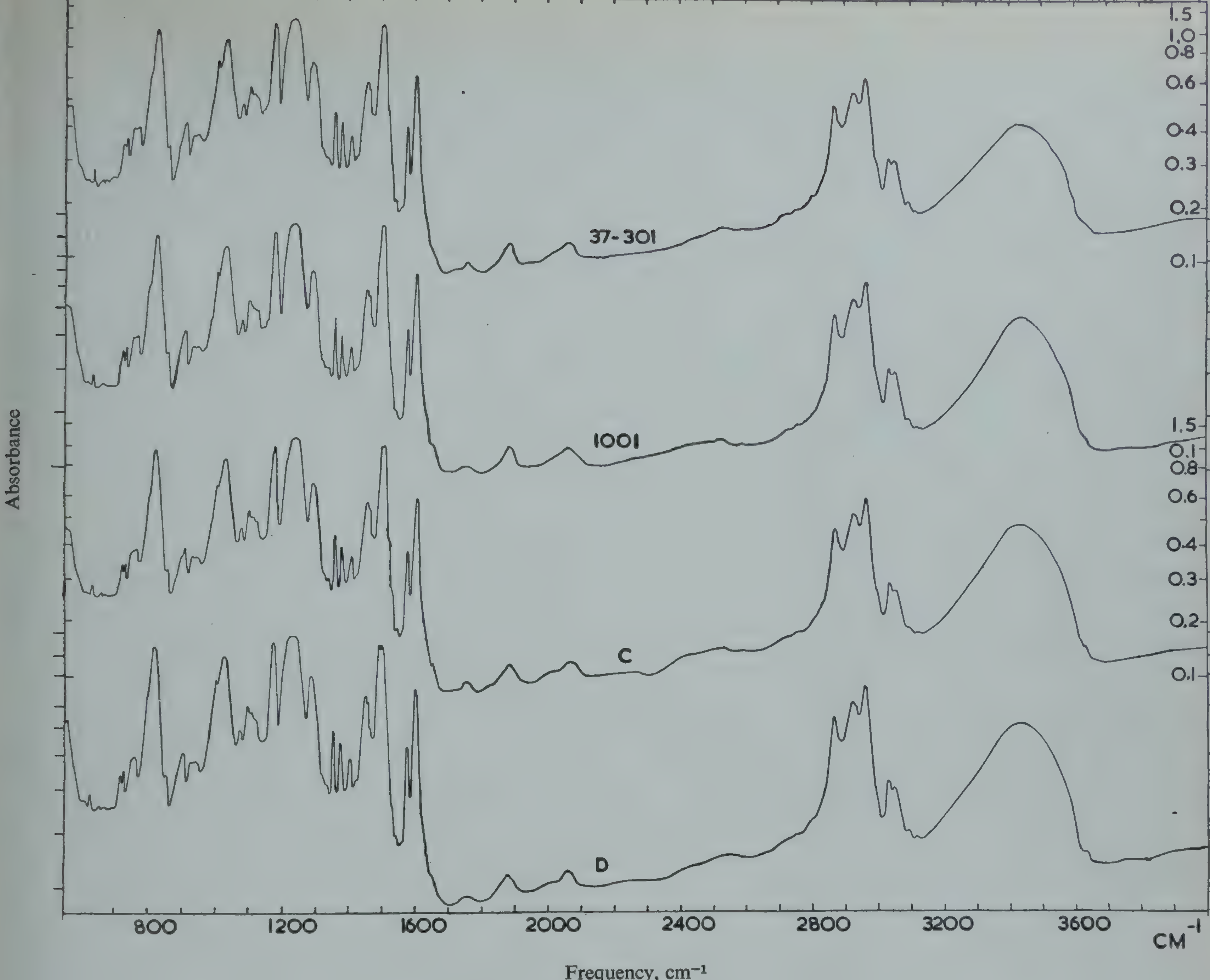


Fig. 2—Infrared Spectra of Solid Epoxy Resins

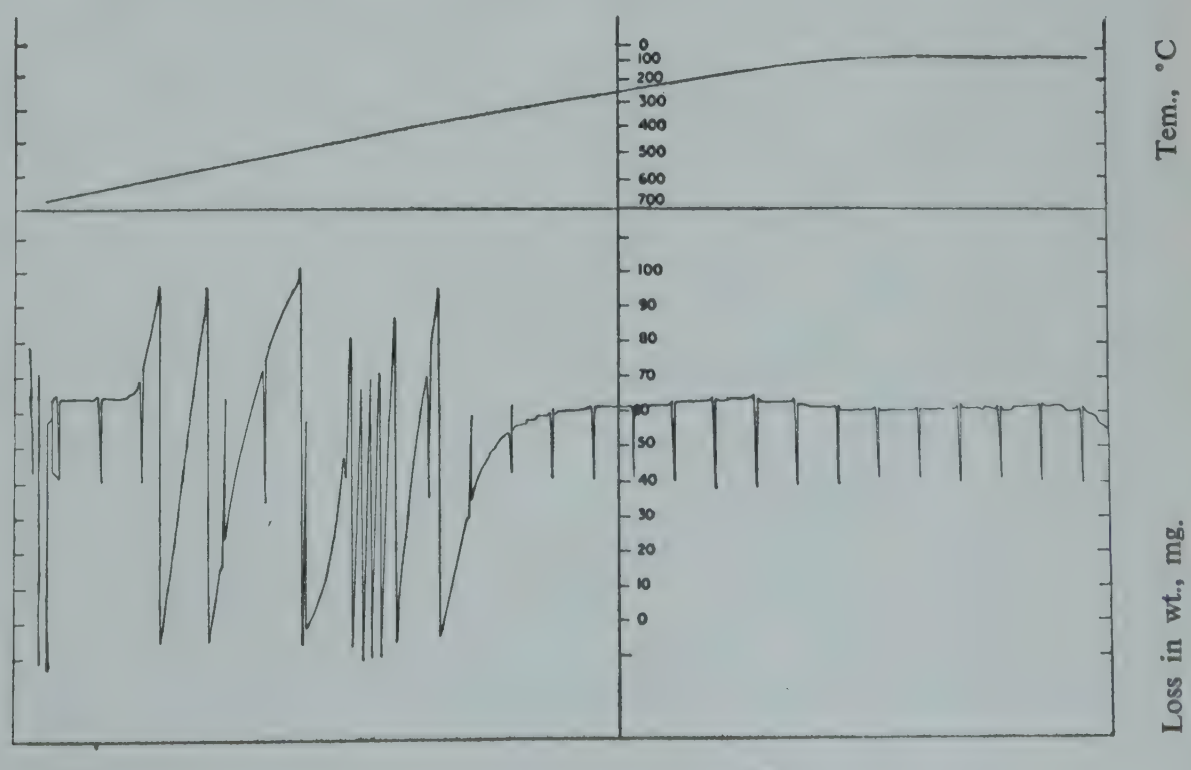


Fig. 3—Heat Treatment of Solid Epoxy Resin G

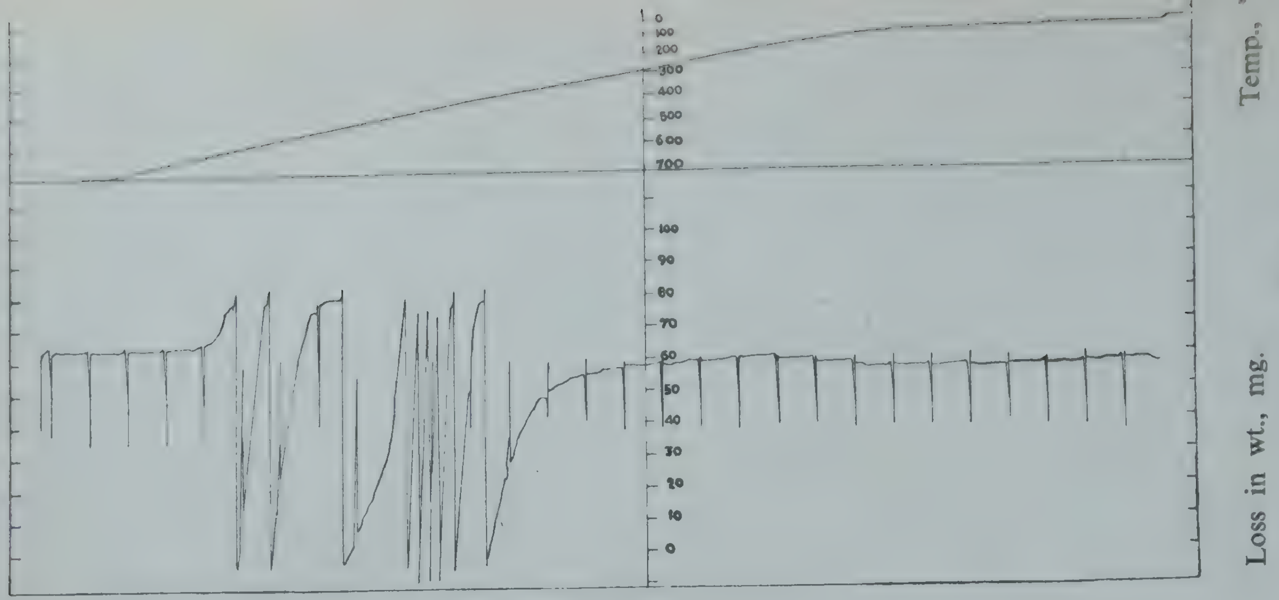


Fig. 4—Heat Treatment of Solid Epoxy Resin Epotuf 37-307

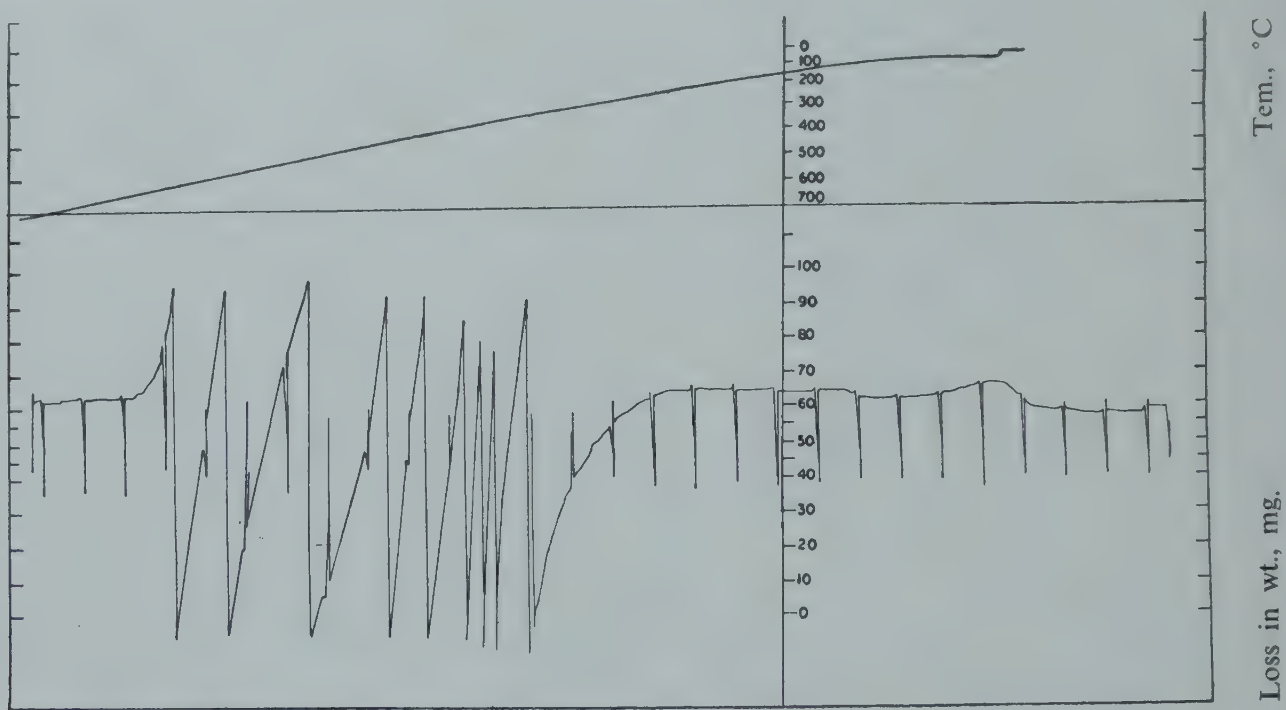


Fig. 5—Heat Treatment of Liquid Epoxide Resin 'A'.

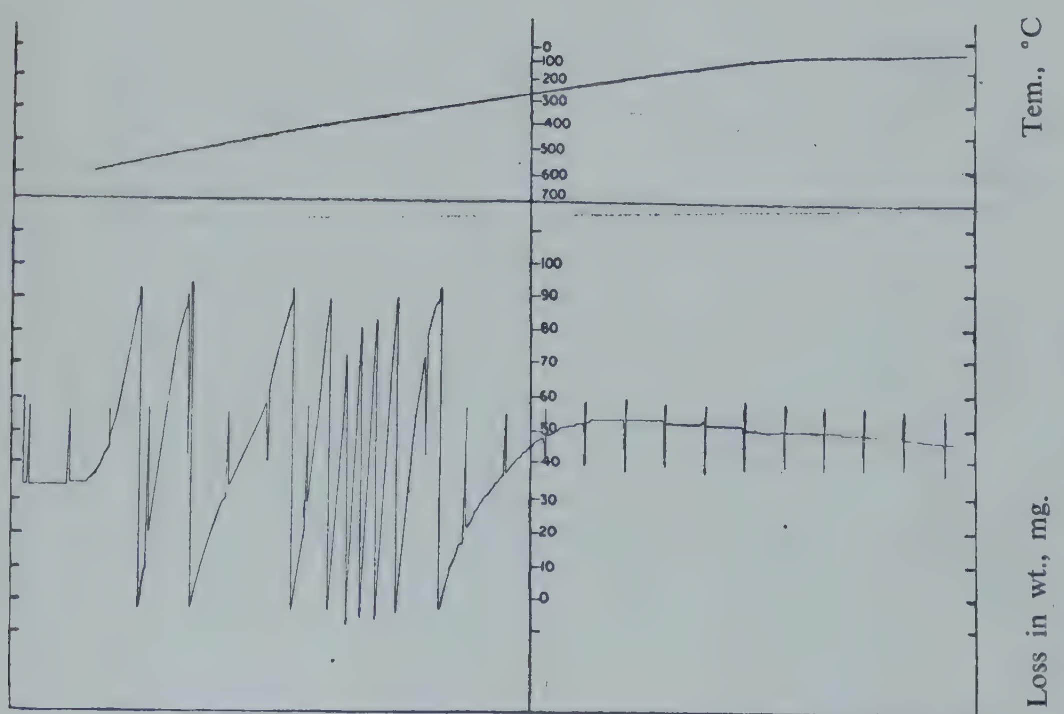


Fig. 6—Heat Treatment of Liquid Epoxide Resin Epotuf 37-140.

It is evident from Figs. 3 and 4 and Table 3 that the thermograms are similar to each other, were rapid loss starting from 390 and 400°C respectively is completed in 40 min. in both the samples, at 615 and 600°C respectively. Other samples are completely evaporated as is evident from columns 'g' and 'h' (Table 3), where the starting and observed weight-losses have been given. Similarly, liquid resins (Figs. 5 and 6) are also comparable to each other.

REFERENCE

1. Gupta, V. S. and Dutta, B K., *Technol.*, 6 (1969), 44.

[Original mss. received on Oct. 3, 1970]

Letter to the Editor

Conversion of Arithmetic Index to Retention Index

Sir,

Methods proposed in the section 5 of the paper entitled "Comparison of Retention and Arithmetic Indices—Their Correlations and Relative Usefulness in Gas Chromatography" published in this issue have been confined to the conversion of retention to the corresponding arithmetic index value. Necessity will no doubt arise for the conversion in the reverse way. For this, the following correlation will form the basis:

$$\log \frac{R_{n+1} - R_n}{R_n - R_{n-1}} = S = \log \frac{R'_{n+1}}{R'_n} \qquad (6)$$

The slope 'S' determined from the uncorrected retention data 'R_n' of any three consecutive normal paraffins or from the plot in Fig. 8A, should be used to build up Fig. 6B, by taking the corrected retention of R'_n as unity, the corresponding value of the next higher n-paraffin being fixed as $\log^{-1} S$ according to equation (6). It has been assumed that the corrected retention data R'_x of any solute 'x' lies between R'_n and R'_{n+1}. R'_x relative to $R'_n=1$ can be determined from its uncorrected counterpart R_x with the help of Fig. 6B. Thus, the relative (corrected) retention data of the solute and the two n-paraffins bracketing it are known. These data are then used to convert I_A to corresponding I values either with (i) a plot similar to Fig. 6A or with (ii) the help of Kovats formula.

It is now clear that the R_n values of the whole series of n-paraffins can be obtained from corresponding data of only three consecutive homologues with the help of equation (6). Thus, I_A can be computed from the R_n values of any three consecutive n-paraffins, while only two consecutive R'_n values are required for the calculation of I.

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Five borehole core samples from South Balanda block of Talcher coalfield have been analysed with a view to use this coal as feedstock in the Talcher fertilizer project. The overall coal from the entire seam contains 16.3—22.4 per cent dry ash on exclusion of bands. The quality and properties of the coals are also similar. The coal ash is highly refractory in nature, but uniform in regard to its chemical composition.

Studies on South Balanda Coal for the Talcher Fertilizer Project

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In view of the limited resources of crudes and natural gas, it is not feasible to base the expansion of fertilizer production in India on them. However, India has large reserves of coal but most of them are high in ash and non-coking. So for developing fertilizer and chemical industries, coal should be given due consideration for its use both as a fuel and a raw material. With the development of new process technology, it has been calculated and seen that coal-based fertilizer plants are sometimes cheaper than the naphtha-based plants, particularly in inland locations[1].

The Union Ministry of Petroleum and Chemicals plan to establish three coal-based fertilizer plants in the public sector has now reached a decisive stage. An expert team of the Planning and Development Division, FCI Ltd. recommends adoption of the Kopper-Totzek process for coal gasification for production of synthesis gas for ammonia. The sites for such plants under consideration are Talcher (Orissa), Ramagundum (A. P.) and Korba (M.P.).

Talcher fertilizer plant with a production target of 900 tonnes of ammonia/day will require about a million tonnes of coal/year. This entire amount will be raised from the South Balanda colliery in the Talcher coalfield, situated at a distance of about 2 km from the proposed fertilizer factory site. A part of this colliery is under mining operation, raising about 40000 tonns/month of coal to satisfy their main customer, viz. the railways and the Talcher Thermal Power Station. The major portion of this vast colliery is still a virgin area. Investigations were, therefore, undertaken for a thorough study of the nature of coal by periodic collection of samples from the actual mining faces, but the most imperative need was to get the correct information of the coal from the virgin area which will be utilized in the production of fertilizer in the future (Fig. 1).

In the past decade, some general studies were made on the coals from Talcher coalfield mainly directed towards production of soft coke for pig iron production[2]. The

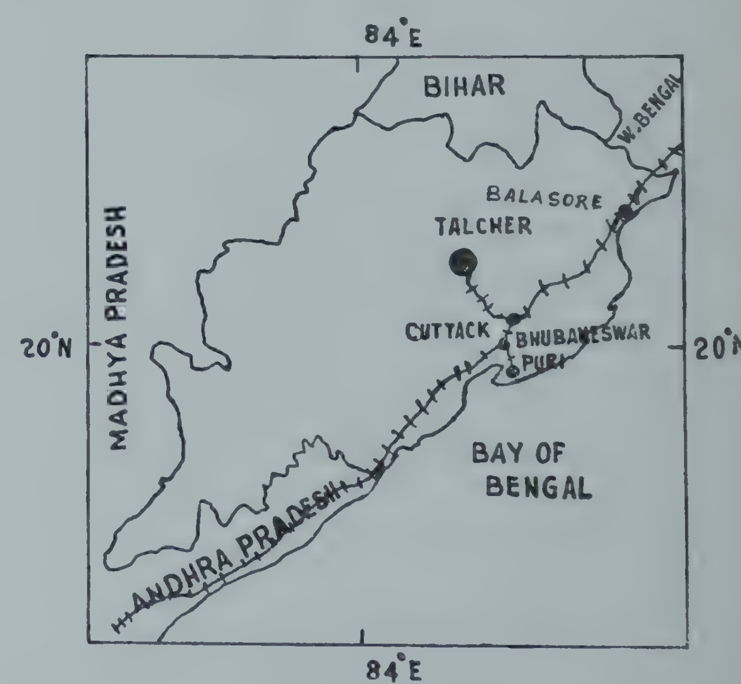

Fig. 1—Map of Orissa Showing Talcher

present utilization of coal for gasification requires extensive studies on the nature of coal ash in regard to its chemical composition and fusion behaviour which were not covered under the earlier work. On the basis of this broad programme, it was absolutely necessary to obtain some borehole samples for complete tests which would assist in predicting the properties of coal and hence the economic utilization of a major quantity of coal in the public sector.

Geology

At present there are three working collieries in the Talcher coalfield, viz. South Balanda, Talcher and Deulbera, all owned by the NCDC. At these collieries, a seam, known as the bottom seam, worked either in full or in part thickness. This seam, which is currently being mined in the South Balanda Colliery, has a thickness varying from 3 metres on the outcrop to 13 metres on the dip side. In the southern part of the South Balanda Colliery it occurs as a single coaly section and records a total thickness around 5 to 7 metres. The seam is almost clean with the occurrence of one or two minor dirt bands. To the dip side in the north, it is progressively attaining a thickness as high as 13 metres (coaly portion only), with some arenaceous shale and sandstone bands dividing it into several coaly sections.

The present working is confined to the south-eastern part of the colliery property by open-cast mining. The area of the colliery property is around 2076 acres. The reserves of the coal in the bottom seam in South Balanda area are as follows:

	Cover lines	Reserves, mil. te.
Under	100′ cover	7.45
Between	100′ & 120′	7.87
Between	120′ & 160′	6.77
Over	160′ cover & Up to F_2F_2 - F_3F_3 faults	5.50
	Total	27.59

Special Borehole Samples

As desired by the FCI, five boreholes spreading over the entire mining block of South Balanda were drilled by the NCDC (Fig. 2). With the data from the analysis of these borehole core samples, it would be possible to work out the long term projections on the ash content and other characteristics of the coal and also provide for the range of variation in the design of the gasifier.

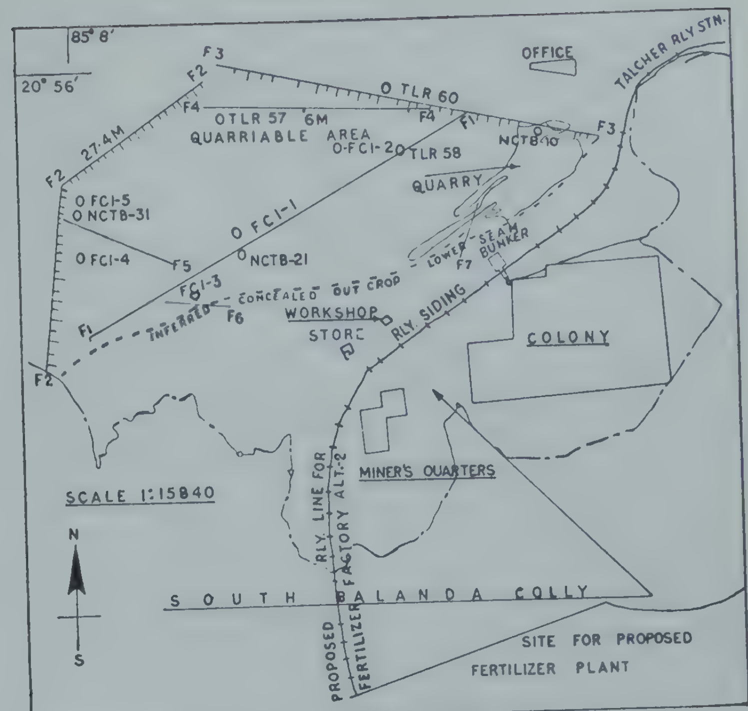

Fig. 2—Location of Five Boreholes in the South Balanda Colliery

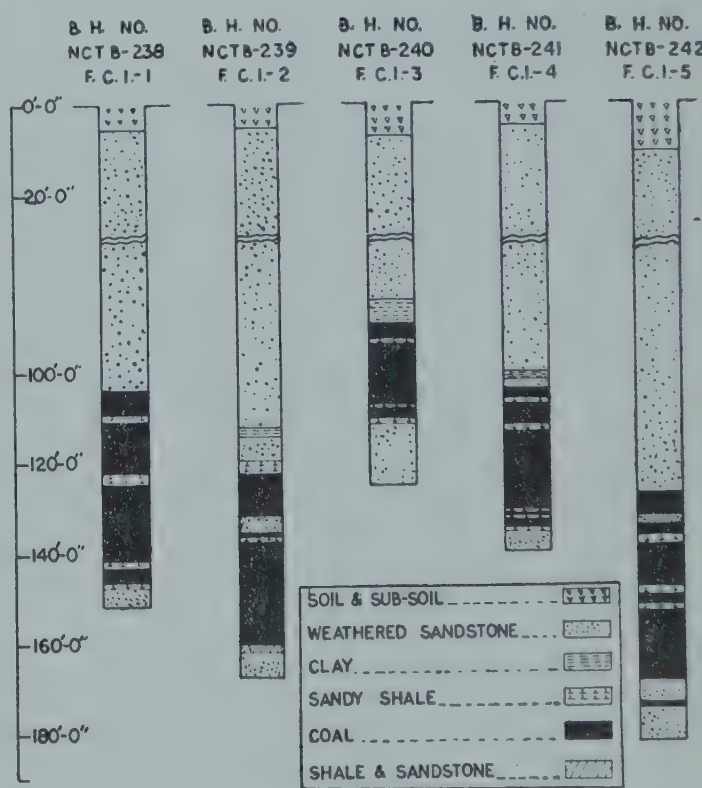

Fig. 3—Log Section of Borehole Core Samples

The special borehole samples are: FCI-1 (NCTB-238), FCI-2 (NCTB-239), FCI-3 (NCTB-240), FCI-4 (NCTB-241) and FCI-5 (NCTB-242). Their log sections are shown in Fig. 3.

Experimental

The borehole cores received from the South Balanda colliery were studied, measured and compared with the log sections supplied by the party (NCDC), and their

lithological characteristics were noted. In the preparation of the samples coaly portions were separated from the shaly portions when the latter exceeded 4″ or more in length. The shaly portions, termed as bands, normally sank, in a liquid of sp. gr. 1.62.

The details of the samples prepared from the coaly portion are given in Table 1A and those of the bands in Table 1B. These bands were analyzed separately for

TABLE 1A—Details of Borehole Core Samples from South Balanda, Talcher

Sample No.	Depth From	Depth To	Thickness	Recovery ft. in	Recovery %	Lithology	Remark
			[Borehole No. NCTB-288 FCI-1]				
PD/TLR-1	103′- 8″	108′- 6″	4′-10″	4′-10″	100	Coal	
PD/TLR-2	110′- 2″	121′- 8″	11′- 6″	11′- 6″	100	Coal	
PD/TLR-3	124′- 1″	141′-10″	17′- 9″	17′- 9″	100	Coal	
PD/TLR-4	142′-11″	146′- 0″	3′- 1″	3′- 1″	100	Coal	
PD/TLR-5 (Average Sample of PD/TLR-1 to 4)	—	—	—	—	—	Coal	PD/TLR-1 13.0% PD/TLR-2 30.9% PD/TLR-3 47.8% PD/TLR-4 8.3%
			[Borehole No. NCTB-239 FCI-2]				
PD/TLR-6	121′-11″	131′- 6″	9′- 7″	9′- 5″	98.3	Coal	
PD/TLR-7	135′- 0″	136′- 2″	1′- 2″	1′- 2″	100	Coal	
	137′- 0″	160′- 1″	23′- 1″	23′- 1″	100	—	
PD/TLR-8 (Average Sample of PD/TLR-6 & 7)	—	—	—	—	—	Coal	PD/TLR-6 28.3% PD/TLR-7 71.7%
			[Borehole No. NCTB-240 FCI-3]				
PD/TLR-9	89′- 3″	89′- 7″	0′- 4″	0′- 4″	100	Shaly Coal	
	89′- 7″	92′- 0″	2′- 5″	2′- 5″	100	Coal	
	92′- 0″	92′- 5″	0′- 5″	0′- 5″	100	Shaly Coal	
PD/TLR-10	92′-10″	102′- 0″	9′- 2″	9′- 2″	100	Coal	
	102′- 0″	103′- 0″	1′- 0″	1′- 0″	100	Shaly Coal	
	103′- 0″	106′- 6″	3′- 6″	3′- 6″	100	Coal	
	106′- 6″	107′- 0″	0′- 6″	0′- 6″	100	Carb. Shale	
PD/TLR-11	107′- 4″	107′- 6″	0′- 2″	0′- 2″	100	Shaly Coal	
	107′- 6″	110′- 0″	2′- 6″	2′- 6″	100	Coal	
	110′- 0″	110′- 2″	0′- 2″	0′- 2″	100	Shaly Coal	
PD/TLR-12 (Average Sample of PD/TLR-9 to 11)	—	—	—	—	—	Coal	PD/TLR-9 15.7% PD/TLR-10 70.3% PD/TLR-11 14.0%
			[Borehole No. NCTB-241 FCI-4]				
PD/TLR-13	103′- 9″	104′- 1″	0′- 4″	0′- 4″	100	Carb. Shale	
	104′- 1″	105′- 9″	1′- 8″	1′- 8″	100	Coal	
	107′- 0″	107′- 2″	0′- 2″	0′- 2″	100	Coal	
	107′- 2″	108′- 0″	0′-10″	0′-10″	100	Carb. Shale	
	108′- 0″	112′- 0″	4′- 0″	4′- 0″	100	Coal	
PD/TLR-14	112′- 9″	113′- 3″	0′- 6″	0′- 6″	100	Carb. Shale	
	113′- 3″	119′- 9″	6′- 6″	6′- 6″	100	Coal	
	119′- 9″	120′- 1″	0′- 4″	0′- 4″	100	Carb. Shale	
	120′- 1″	122′- 6″	2′- 5″	2′- 5″	100	Coal	
	122′- 6″	122′- 9″	0′- 3″	0′- 3″	100	Carb. Shale	
	122′- 9″	123′- 6″	0′- 9″	0′- 9″	100	Shaly Coal	
	123′- 6″	130′- 6″	7′- 0″	7′- 0″	100	Coal	
PD/TLR-15	131′- 1″	131′- 7″	0′- 6″	0′- 6″	100	Coal	
	131′- 7″	132′- 0″	0′- 5″	0′- 5″	100	Shaly Coal	
	132′- 0″	132′- 3″	0′- 3″	0′- 3″	100	Coal	
	132′- 7″	134′- 6″	1′-11″	1′-11″	100	Coal	
PD/TLR-16 (Average Sample of PD/TLR-13 to 15)	—	—	—	—	—	Coal	PD/TLR-13 25.1% PD/TLR-14 63.8% PD/TLR-15 11.1%

TABLE 1A—DETAILS OF BOREHOLE CORE SAMPLES FROM SOUTH BALANDA, TALCHER—(Contd.)

Sample No.	Depth From	Depth To	Thickness	Recovery ft. in	Recovery %	Lithology	Remark
			[Borehole No. NCTB-242, FCI-5]				
PD/TLR-17	127′- 5″	127′- 8″	0′- 3″	0′- 3″	100	Sandy coal	
	127′- 8″	133′- 1″	5′- 5″	5′- 5″	100	Coal	
	134′- 8″	137′- 6″	2′-10″	2′-10″	100	Coal	
PD/TLR-18	138′- 8″	139′- 8″	1′- 0″	1′- 0″	100	Coal	
	139′- 8″	140′- 0″	0′- 4″	0′- 4″	100	Carb. Shale	
	140′- 0″	149′- 4″	9′- 4″	9′- 4″	100	Coal	
	150′- 8″	152′- 7″	1′-11″	1′- 11″	100	Coal	
PD/TLR-19	153′- 2″	169′- 8″	16′- 6″	16′- 6″	100	Coal	
PD/TLR-20 (Average Sample of PD/TLR-17 to 19)	—	—	—	—	—	Coal	PD/TLR-17 22.4% PD/TLR-18 33.6% PD/TLR-19 44.0%

TABLE 1B—DETAILS OF SHALE BANDS ASSOCIATED WITH THE BOREHOLE COAL-CORES

Sample No.	Depth, ft. in. From	Depth, ft. in. To	Thickness, ft. in.	Recovery ft. in.	Recovery %	Lithology
			Borehole No. NCTB 238, FCI-1			
PD/TLR-21	108′- 6″	110′- 2″	1′- 8″	1′- 8″	100	Sandy shale
PD/TLR-22	121′- 8″	124′- 1″	2′- 5″	2′- 5″	100	Alternate bands of shale and sandstone
PD/TLR-23	141′-10″	142′-11″	1′- 1″	1′- 1″	100	Shale
			Borehole No. NCTB 239, FCI-2			
PD/TLR-24	131′- 6″	135′- 0″	3′- 6″	3′- 6″	100	Alternate bands of shale and sandstone
PD/TLR-25	136′- 2″	137′- 0″	0′-10″	0′-10″	100	Grey to sandy shale
			Borehole No. NCTB 240, FCI-3			
PD/TLR-26	92′- 5″	92′-10″	0′- 5″	0′- 5″	100	Alternate bands of shale and sandstone
PD/TLR-27	107′- 0″	107′- 4″	0′- 4″	0′- 4″	100	Alternate bands of shale and sandstone
			Borehole No. NCTB 241, FCI-4			
PD/TLR-28	105′- 9″	107′- 0″	1′- 3″	1′- 3″	100	Sandy shale
PD/TLR-29	112′- 0″	112′- 9″	0′- 9″	0′- 9″	100	Clay and grey shale
PD/TLR-30	130′- 6″	131′- 1″	0′- 7″	0′- 7″	100	Grey shale
PD/TLR-31	132′- 3″	132′- 7″	0′- 4″	0′- 4″	100	Grey shale
			Borehole No. NCTB 242, FCI-5			
PD/TLR-32	133′- 1″	134′- 8″	1′- 7″	1′- 7″	100	Alternate bands of shale and sandshale
PD/TLR-33	137′- 6″	138′- 8″	1′- 2″	1′- 2″	100	Grey sandy shale
PD/TLR-34	149′- 4″	150′- 8″	1′- 4″	1′- 4″	100	Sandy shale
PD/TLR-35	152′- 7″	153′- 2″	0′- 7″	0′- 7″	100	Sandy shale

moisture, ash and volatile matter contents. Overall samples from the boreholes (coaly portion only) were prepared by mixing different coal sections of the same borehole in the same proportion of their respective lengths. Recovery of the cores were 100 per cent in all cases except one.

Analysis of Samples and Their Ashes: Each of the samples (Table 1A) was tested for proximate analysis, ultimate analysis, calorific value and ash fusion temperature. Table 2 gives proximate analysis of the samples on air-dry, dry and dry ash-free basis. In Table 3 ultimate analysis and calorific value are shown. The various characteristics of the fusion temperature of coal ashes were determined under a mildly reducing atmosphere (steam and hydrogen in equal proportions), with ash pellets placed on a platinum foil instead of on a ceramic tile and heated in the Lietz's apparatus. The results are given in Table 4. The composition of the coal ash was determined only for the average of each borehole sample (Table 5). The proximate analysis of the shaly coal and carbonaceous shales associated with the boreholes are given in Table 6.

Discussion

It is seen from Table 2 that dry ash contents of the full core (excluding band) are 17.3 and 16.3 per cent for borehole samples FCI-1 and FCI-2. In the case of other borehole cores, the dry ash contents are higher reaching a maximum of 22.4 per cent in the case of FCI-5. In the cases of FCI-1, 2 and 4, a major portion of the cores contains low ash coal. Thus, in FCI-1, 47.8 per cent of the borehole coal has 14.9 per cent dry ash; in FCI-2, 71.7 per cent of the coal has 14.7 per cent dry ash and in FCI-4, 63.8 per cent has 15.6 per cent dry ash. In borehole sample 3, dry ash content of the various cross sections separated ranged from 19.5 to 25.9 per cent. In the case of borehole sample 5, this ranged between 19.8 and 24.9 per cent.

The moisture contents of the air-dried average borehole samples ranged from 8.4 to 10.2 per cent; the same

TABLE 2—Analysis of Borehole Coal Samples (Proximate Analysis)

Sample No.	Air-dried Sample (−72 mesh)				Dry Basis			D.a.f. Basis	
	Moist %	Ash %	V.M. %	F.C. %	Ash %	V.M. %	F.C. %	V.M. %	F.C. %
PD/TLR-1	10.3	18.2	28.9	42.6	20.3	32.2	47.5	40.4	59.6
PD/TLR-2	9.2	18.0	29.5	43.3	19.8	32.5	47.7	40.5	59.5
PD/TLR-3	9.9	13.4	32.7	44.0	14.9	36.3	48.8	42.7	57.3
PD/TLR-4	11.7	15.1	33.8	39.4	17.1	38.3	44.6	46.2	53.8
PD/TLR-5	9.1	15.7	31.0	44.2	17.3	34.1	48.6	41.2	58.8
PD/TLR-6	8.6	18.2	29.0	44.2	19.9	31.7	48.4	39.6	60.4
PD/TLR-7	9.7	13.3	33.3	43.7	14.7	36.9	48.4	43.2	56.8
PD/TLR-8	9.2	14.8	32.3	43.7	16.3	35.3	48.1	42.5	57.5
PD/TLR-9	11.8	20.5	32.1	35.6	23.2	36.4	40.4	47.4	52.6
PD/TLR-10	9.4	17.7	33.4	39.5	19.5	36.9	43.6	45.8	54.2
PD/TLR-11	8.6	23.7	33.2	34.5	25.9	36.3	37.8	49.0	51.0
PD/TLR-12	9.4	19.0	33.6	38.0	21.0	37.1	41.9	46.9	53.1
PD/TLR-13	9.1	20.3	27.1	43.5	22.3	29.8	47.9	38.4	61.6
PD/TLR-14	11.7	13.8	31.8	42.7	15.6	36.0	48.4	42.7	57.3
PD/TLR-15	8.4	27.7	30.6	33.3	30.2	33.4	36.4	47.9	52.1
PD/TLR-16	10.2	17.1	30.4	42.7	19.0	33.9	47.1	41.8	58.2
PD/TLR-17	9.2	18.8	32.5	39.5	20.7	35.8	43.5	45.1	54.9
PD/TLR-18	9.1	18.0	27.6	45.3	19.8	30.3	49.9	38.0	62.0
PD/TLR-19	8.4	22.8	30.5	38.3	24.9	33.3	41.8	44.3	55.7
PD/TLR-20	8.4	20.5	30.0	41.1	22.4	32.7	44.9	42.2	57.8

TABLE 3—ANALYSIS OF BOREHOLE COAL SAMPLES

[Ultimate Analysis and Calorific Value]

Sample No.	Ultimate Analysis (air-dry basis)							Gross Calorific Value, K.Cal/kg.		
	Moist, %	Ash, %	Carbon, %	Hydrogen, %	Sulphur, %	Nitrogen, %	Oxygen (by diff.) %	Air-dried Basis	Dry Basis	d.a.f. Basis
PD/TLR-1	10.3	18.2	55.43	3.52	0.42	—	—	5510	6150	7710
			(77.91)	(4.94)	(0.45)	—	—	—	—	—
PD/TLR-2	9.2	18.0	56.71	3.72	0.35	—	—	5470	6110	7510
			(78.71)	(5.12)	(0.38)	—	—	—	—	—
PD/TLR-3	9.9	13.4	59.03	3.86	0.44	—	—	5970	6620	7780
			(76.96)	(5.04)	(0.48)	—	—	—	—	—
PD/TLR-4	11.7	15.1	55.91	3.78	0.98	—	—	5550	6290	7580
			(76.38)	(5.15)	(1.06)	—	—	—	—	—
PD/TLR-5	9.1	15.7	58.55	4.08	0.43	1.21	10.93	5660	6300	7530
			(77.72)	(5.42)	(0.47)	(1.61)	(14.78)	—	—	—
PD/TLR-6	8.6	18.2	58.64	3.78	0.36	—	—	5550	6080	7580
			(80.10)	(5.17)	(0.39)	—	—	—	—	—
PD/TLR-7	9.7	13.3	61.06	4.12	0.39	—	—	5960	6580	7730
			(79.30)	(5.36)	(0.42)	—	—	—	—	—
PD/TLR-8	9.2	14.8	60.20	3.98	0.42	1.30	10.10	5810	6410	7640
			(79.20)	(5.23)	(0.47)	(1.66)	(13.44)	—	—	—
PD/TLR-9	10.1	20.9	51.94	3.48	0.66	—	—	5010	5580	7270
			(76.80)	(5.14)	(0.73)	—	—	—	—	—
PD/TLR-10	8.4	18.1	55.64	3.68	0.85	—	—	5600	6110	7610
			(76.33)	(5.04)	(0.93)	—	—	—	—	—
PD/TLR-11	6.8	24.3	52.06	3.42	0.51	—	—	5220	5600	7570
			(76.83)	(5.05)	(0.54)	—	—	—	—	—
PD/TLR-12	7.2	19.8	54.70	3.61	0.61	1.32	12.76	5560	5990	7610
			(76.42)	(5.05)	(0.67)	(1.81)	(16.05)	—	—	—
PD/TLR-13	8.2	20.5	56.86	3.14	0.29	—	—	5410	5890	7580
			(79-63)	(4.40)	(0.31)	—	—	—	—	—
PD/TLR-14	9.7	14.2	60.15	3.92	0.50	—	—	5900	6530	7750
			(78.94)	(5.15)	(0.55)	—	—	—	—	—
PD/TLR-15	7.2	28.0	50.11	3.43	0.58	—	—	4870	5250	7540
			(77.30)	(5.28)	(0.62)	—	—	—	—	—
PD/TLR-16	8.7	17.4	58.09	3.60	0.39	1.26	10.56	5670	6210	7670
			(78.61)	(4.88)	(0.43)	(1.70)	(14.38)	—	—	—
PD/TLR-17	8.5	18.9	51.86	3.47	0.43	—	—	5600	6110	7710
			(78.32)	(4.78)	(0.47)	—	—	—	—	—
PD/TLR-18	8.5	18.4	59.20	3.54	0.37	—	—	5640	6160	7730
			(80.77)	(4.84)	(0.40)	—	—	—	—	—
PD/TLR-19	6.4	23.3	53.85	3.49	0.48	—	—	5270	5630	7760
			(77.48)	(5.02)	(0.51)	—	—	—	—	—
PD/TLR-20	7.2	20.8	56.56	3.71	0.33	1.17	10.23	5490	5920	7630
			(78.67)	(5.16)	(0.35)	(1.63)	(14.19)	—	—	—

N.B. Figures in the parenthesis refer to analysis on d.a.f. basis.

TABLE 4—FUSION TEMPERATURE OF ASH OF BOREHOLE COAL SAMPLES

Sample No.	Ash Fusion Temp. °C (under mild reducing atmosphere)		
	Initial Deformation Temp.	Softening Temperature	Flow Temperature
PD/TLR-1	Not Sharp	>1450	>1450
PD/TLR-2	Not Sharp	>1450	>1450
PD/TLR-3	1380	>1450	>1450
PD/TLR-4	Not Sharp	>1450	>1450
PD/TLR-5	1400	>1450	>1450
PD/TLR-6	1410	>1450	>1450
PD/TLR-7	1310	>1450	>1450
PD/TLR-8	1350	>1450	>1450
PD/TLR-9	1220	1460	>1460
PD/TLR-10	1320	>1450	>1450
PD/TLR-11	Not Sharp	>1450	>1450
PD/TLR-12	1300	>1450	>1450
PD/TLR-13	1350	>1450	>1450
PD/TLR-14	1220	>1450	>1450
PD/TLR-15	Not Sharp	>1450	>1450
PD/TLR-16	1360	>1450	>1450
PD/TLR-17	1310	>1450	>1450
PD/TLR-18	Not Sharp	>1450	>1450
PD/TLR-19	1250	1340	1430
PD/TLR-20	1320	>1450	>1450

TABLE 6—PROXIMATE ANALYSIS OF SHALY COAL AND CARBONACEOUS SHALES ASSOCIATED WITH BOREHOLE COAL CORE

Sample No.	Proximate Analysis of Air-dried Samples			
	Moisture, %	Ash, %	V. M., %	F. C., %
PD/TLR-21	2.6	65.4	17.6	14.4
PD/TLR-22	1.0	86.7	9.0	3.3
PD/TLR-23	1.3	83.0	10.6	5.1
PD/TLR-24	1.0	87.5	8.8	3.7
PD/TLR-25	1.5	84.5	9.9	4.1
PD/TLR-26	1.6	78.2	13.0	7.2
PD/TLR-27	0.7	89.4	8.8	1.1
PD/TLR-28	2.5	66.6	17.2	13.7
PD/TLR-29	1.4	82.7	10.2	5.7
PD/TLR-30	1.5	79.5	11.9	7.1
PD/TLR-31	1.3	72.8	16.8	19.3
PD/TLR-32	1.3	76-5	13.8	8.4
PD/TLR-33	1.4	78.9	12.4	7.3
PD/TLR-34	1.2	85.5	9.1	4.2
PD/TLR-35	1.4	82.1	10.3	6.2

of the air-dried samples have been noticed to have a seasonal variation. Such a variation is shown in the moisture values of some samples in Tables 2 and 3. In Table 2, the samples were analyzed in September, whereas in Table 3 the values which differed were determined in December. The volatile matter of the overall core samples ranged from 41.2 to 46.9 per cent on dry ash-free basis. The coal is non-caking in character (caking index < 5).

Calorific value of the samples on dry ash-free basis is fairly uniform (7510-7780 cal/g.). Thus, from Fig. 4 calorific value of any sample can be obtained from a knowledge of ash and moisture contents.

The coals from South Balanda colliery are characterized by low carbon (76.4-79.2 per cent) and hydrogen (4.9-5.4 per cent) contents the analyses in both the cases being given for the overall samples on d.a.f. basis. Total sulphur ranged from 0.35 to 0.67 per cent and nitrogen from 1.61 to 1.81.

The ash of the South Balanda coal is in general refractory in nature. Its fusion temperature is very high (Table 4), and the results so far obtained indicate that

TABLE 5—ANALYSIS OF ASH IN THE AVERAGE FULL LENGTH BOREHOLE COAL SAMPLES

Sample No.	SiO_2, %	$Al_2O_3+TiO_2$, %	Fe_2O_3, %	CaO, %	MgO, %	SO_3, %	Alkalies (by diff.), %
PD/TLR- 5	57.90	29.20	8.40	1.88	0.99	1.23	0.40
PD/TLR- 8	56.67	27.45	12.80	1.59	0.20	1.05	0.24
PD/TLR-12	54.50	28.50	13.60	1.54	0.00	1.26	0.60
PD/TLR-16	56.96	30.70	7.20	1.89	0.99	1.23	1.03
PD/TLR-20	56.40	28.20	12.40	1.12	0.00	1.06	0.82

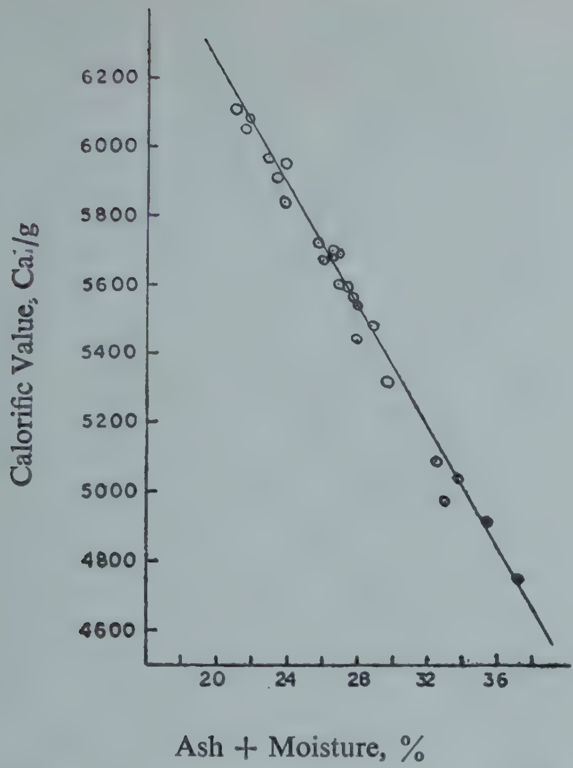

Fig. 4—Ash and Moisture Vs Calorific Value

TABLE 7—ANALYSIS OF R.O.M. AND STEAM COALS

	R.O.M. Coal	Steam Coal
Proximate Analysis		
Moisture	10.3	11.2
Ash	15.4	11.7
Volatile matter	31.3	32.0
Fixed carbon	43.0	45.1
Ultimate Analysis (d.a.f. basis), %		
Carbon	78.60	79.10
Hydrogen	5.40	4.88
Sulphur	0.56	0.52
Nitrogen	1.80	1.80
Oxygen	13.64	13.70
Calorific Value, K Cal/kg.		
Air-dried basis	5680	5970
d.a.f. basis	7650	7750
Ash Fusion Characteristics, °C (under mild reducing atmosphere)		
Initial deformation	1320	1260
Fusion	>1450	1440
Flow	>1450	>1450

the initial deformation temperature in most cases is above 1200°C. and the softening temperature above 1450°C, even under mildly reducing atmosphere.

The ashes of only the overall coal samples have been analysed. Their composition (Table 5) shows that silica is fairly uniform but ferric oxide varied from 7.2 to 13.6 per cent. Their high fusion temperatures are due to high alumina and low lime and magnesis contents. It is therefore, necessary to add lime or other fluxing agents to bring down the fusion temperature of the ash.

All the shales are high is ash content (Table 6), mostly around 80 per cent; and if not properly picked up may increase ash content of the coal.

Because of the nature of open cast mining having a large amount of overburden above the coal seam, there is every reason for the coal being mined with extraneous dirt, particularly sand. The contamination may be maximum in the rainy season. At present the r.o.m. coal after mining is screened to three size fractions, viz. steam (8″—1′/2″), nut (1½″-⅝″) and black coal (below 5/8″). A typical analysis of a steam and r.o.m. samples collected during the rainy season from the working face is given in Table 7. The results show that by screening the r.o.m. coal over 1½″ screen may produce steam coal (to the extent of 70 per cent) in which the air-dried ash has fallen from 15.4 to 11.7 per cent. Thus, screening of the r.o.m. coal may help to lower its ash percentage. Free silica when present in the coal is detrimental to the crushers for pulverizing the coal to the optimum fineness. By screening it may be possible to remove a major part of the free silica.

Conclusion

Overall analysis of the coal cores from different boreholes has given a complete picture for its use in gasification by the Kopper-Totzek process. It shows that at different positions, the percentage of ash has been different; but regarding the quality of ash there is a good uniformity. Previous analysis of borehole samples from the nearby places compares favourably with this present study. Thus, in general the coal ash is highly refractory in nature and as such the coal is unsatisfactory for gasification. In requires blending with fluxing agent; further work is in progress in this line.

Acknowledgements

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Technical Digests

Potassium Sulphate from Sea Bittern

There is no natural deposit of potash in India except a few surface patches of potassium nitrate in UP and Bihar. At present all the potash salts are imported. However, sea-water is a potential source. The bitterns left over after recovery of common salt from solar evaporation of sea water leave a residue known as 'mixed salt' which has the following composition (per cent by weight): sodium chloride 18-24, potassium chloride 18-24, magnesium sulphate 30-32, magnesium chloride 3-4 and water 20-22.

There is a well-known process for obtaining carnallite (KCl. Mg Cl_2.6 H_2O) from the mixed salt by extraction with hot magnesium chloride solution and subsequent recovery of potassium chloride by leaching with water. There is a froth flotation technique for obtaining Schoenite (K_2 SO_4. Mg SO_4. $6H_2O$) which, on further processing with potassium chloride in water medium, gives potassium sulphate. The recovery is, however, limited by the solubility of both potassium sulphate and potassium chloride in water medium. The yield is, however, not high as the precipitation is not complete.

This Division of FCI Ltd. has developed a process* of separating sodium and magnesium chlorides from the mixed salt using a methanol-water solution yielding a sulphate-enriched crop containing sulphate of potassium and magnesium; later, most of the sulphate is precipitated in the form of potassium sulphate by the addition of potassium chloride and methanol to a solution of the sulphate-enriched crop utilizing the low solubility of potassium magnesium sulphate and potassium sulphate in methanol-methanol water solution.

The process comprises of the following steps: (1) crushing of mixed salt to the desired size preferably to pass through 60 mesh (BSS).

(2) Pulping the crushed mixed salt with the methanol-water solution containing magnesium chloride, the optimum concentration of which is in the range of 5-6 per cent w/v with or without other minor ingredients, like sodium chloride, potassium chloride and mgnesium sulphate not exceeding 0.5-0.9, 0.4-0.8 and 1-2 per cent w/v respectively, thereby extracting the sodium and magnesium chlorides present in the mixed salt and also a part of magnesium present as sulphate in the mixed salt in the form of magnesium chloride.

(3) Centrifuging the above slurry which leaves a sulphate-enriched crop of potassium and magnesium sulphate analysing (per cent) as follows: sulphate 45-47, potassium 18-20, magnesium 6-8, sodium 1-2 and chlorine 4-6, having the following approximate composition (per cent) air-dried at 110°C; potassium sulphate 42-44, magnesium sulphate 27-29, magnesium chloride 1-5 and water 20-25.

(4) Bringing into solution the sulphate-enriched potassium and magnesium sulphate crop with the addition of minimum quantity of water and clarifying the solution with a flocculating agent, like alum, ferrous sulphate or starch, to remove clayey matter followed by the addition of the required quantity of potassium chloride resulting in the precipitation of a little quantity of potassium sulphate.

Methanol is added to this liquor/slurry bringing the concentration of the former in the total volume to 50 per cent (v/v) when almost 90-95 per cent of the potassium and sulphate ions present precipitate out potassium sulphate having a purity of 92-95 per cent. This crop is centrifuged and washed with a saturated potassium sulphate solution, thus enhancing the purity of potassium sulphate to 96-98 per cent.

(5) The methanol-water solution after the separation of potassium sulphate crop from above (under step 4) is added to the extraction vessel for subsequent separation of the sulphate-enriched potassium and magnesium crop from mixed salt. The above methanolic solution has the following composition (per cent): magnesium chioride 5-6, magnesium sulphate 0.4-0.8, potassium sulphate 0.15-0.2, potassium chloride 0.15-0.2.

(6) The mother liquor from step 5 is distilled and the methanol is reused in the process.

* Indian Patent No. 119592—A Process for the Recovery of Potassium and Sulphate Ions as Potassium Sulphate from Saline Deposits, Particularly Mixed Salts left over after Solar Evaporation of Waste Bitterns from Common Salt Industry by S. Ranganathan and J. M. Sarkar

Lectures & Reviews

Fertilizer Plant Manufacture* in India

In order to achieve self-sufficiency, Fertilizer Corporation of India took a lead to encourage indigenous fabricators to manufacture such items of equipment for their Durgapur and Cochin projects which could be done in this country. The scope drawings and specifications, for various type of equipment were secured by FCI from their foreign collaborator, Montecatini of Italy. In India there are now a number of workshops of various types, size and description for fabricating equipment needed, such a storage tanks, bins and hoppers, cyclone separators, gas holders, etc., for fertilizer and chemical industries. A dozen of shops can fabricate medium size equipment, such as reaction vessels, mixtures, and blenders, extractors, scrubbers, vaporizers, compartment dryers, etc. Five or six heavy workshops can now manufacture highly sophisticated and complicated heavy vessels and equipment such as high pressure vessels including boilers absorption columns, distillation columns, heat exchangers and superheaters, evaporators crystallizers and rotary dryers and calciners. For a typical fertilizer complex, equipment consisting of pressure vessels, heat exchangers, fired heaters, reactors, converters form about 50 per cent of the investment. World Bank has now accepted that India can now fabricate upto 70 per cent of the equipment needed for nitrogenous fertilizer plants. While in the Durgapur project the value of indigenous equipment is of the order of Rs. 7 crores out of a total investment of Rs. 46 crores, in the Talcher or Ramagundam project the foreign exchange need has dropped to only Rs. 19 crores out of a total investment of Rs. 70 Crores.

The types of equipment required for the fertilizer and chemical industries are as follows: vessels and heat exchangers; steam-raising and waste heat boilers; pipes and pipe fittings; valves; conveyors and elevators; pumps, compressors and blowers; furnaces; crushers and grinders; and air separation plants. At a meeting organized by the DGTD in January 1969 for a dialogue for the chemical, fertilizer and petrochemical industries which was attended by 36 representatives of the various fertilizer and allied projects, plant and equipment manufacturers and 23 consultancy firms elaborate shopping lists were prepared by Engineers India Ltd. and the Indian Farmers Fertilizer Coop. Ltd. and discussed in detail to ascertain the items which could be manufactured by the indigenous fabricators.

One matter of prime consideration for the use of indigenous equipment is that the supply of such equipment must be effected within the prescribed time schedule so as not to delay the completion of the project; for ascertaining the cause of such delays, the Government has appointed a committee whose report can be a guideline for future projects. This report is under preparation. In this connexion it must be emphasized that the project authorities concerned should talk with the manufacturers sufficiently ahead of time about their requirements so that all questions of timely procurement of raw materials, proper scheduling and allocation of shop capacity, etc. can be so planned as not to delay the project.

Another difficulty faced by plant manufacturers is that for some specialized 'tailor-made' items the project authorities are not able to give them detailed fabrications drawings, and at best only broad specifications and dimensioned sketches are made available. Because of this limitations, only a few shops in India are in a position to use this meagre information to work out detailed fabrication shop drawings for customers' approval. Some kind of a solution has to be found to fill this gap by making available a limited amount of foreign exchange for the purchase of drawings and know-how for certain specialized tailor-made equipment from abroad. In the field of heat exchangers a great deal of expertize has been built up in this country but still there is a gap of preparing design calculation for thermal ratings using computerized programmes; in this direction a lead has been taken by Engineers India Ltd.

For executing fertilizer projects in time, various Government authorities should be urged to set time limits for various matters connected with the projects right from the feasibility report stage till the plant goes into operation. Furthermore, raw materials needed,

* Lecture on 'Indigenous Fertilizer Plant Manufacture—Problems and Prospects' by D. N. Daruvalla, delivered on Aug. 20, 1970 at the Fertilizer Institute, Fertilizer Assn. of India, New Delhi.

which are in short supply and take a long time to secure from foreign suppliers, should be made available to indigenous manufacturers in time. For this, special licences may be given either to project authorities or to the indigenous manufacturer for timely procurement of these raw materials.

In the initial stage of a project exact lists of many items cannot be prepared because no final drawings can be made. Thus, there is a need for flexibility and relaxation of the rigid procedures adopted by the DGTD and the Government for granting licences for raw material procurement. Some machinery will have to be evolved by the Government to ensure that a clear cut decision is given as to which items have to be imported and which have to be manufactured indigenously.

Dr. Daruvalla presented case studies of two problems —first, stage distiller and ammonia condenser for urea plant encountered by the project authorities and the indigenous manufacturers for the manufacture of fertilizer plant equipment.

Ecology of Research and Development

Under the auspices of the FCI Engineers' and Scientists' Association, Dr. P. N. Mukherjee, Asst. Director, Central Fuel Research Institute, Jealgora (Dhanbad), delivered an interesting lecture on the 'Impact of Society on Science and Technology in India' on March 27, 1971.

As creations of human intellect, science and technology are social products, it follows then that there must be an intimate relation between science and society. To understand the ecology of research, we have to consider the social conditions as well as the traditions and ideologies which will prevail in society. In so far as Indian society is concerned, its influence on science may be conveniently examined from the following standpoints.

(a) *Social Demand*: If there is persistent demand on the part of the society, technological developments take place in an extremely short time. Time and again this has been observed in western countries—specially during war-time emergencies. The modern industrial nations are motivated by an urge for greater material comfort and higher standard of living. In India, on the contrary, society is guided by spiritual ideals which positively discourage research after greater material comfort. Both Tagore and Gandhiji gave expression to their inherent distrust for machine-based industrial civilization. It seems doubtful if Indian society is psychologically oriented for rapid industrial development even at this stage.

(b) *Social Understanding*: The material conveniences which result from application of science are understood and appreciated by the society which has, however, little understanding about the complex process through which scientific knowledge ultimately reaches the society in the form of technological application. The primary business of science is to gather, classify and collate basic knowledge which at a certain stage becomes ripe for commercial application. Much of confusion that exists in India regarding the role of science in society stems from an over-emphasis on the material benefits of science in disregard to the basis on which application of science depends. We are yet to realise that pure science does not remain pure indefinitely. Sooner or later it is apt to turn into applied science and finally to technology. If scientists expect support from the society for their very existence, then they are under moral obligation to make intelligible to the society the method by which science functions for the welfare of the society. A lack of understanding will inevitably thwart the progress and development of science and technology.

(c) *Authoritarian Society*: By age-long tradition Indian society is authoritarian in outlook. It demands submission to the authority—be it of age, culture, tradition or office. The effect of the authoritarian attitude is indeed demoralising for the growth of scientific spirit and tradition which demands freedom of thought, liberation from superstition and taboo, from authority and dictation and freedom from concept of infallibility and inerrability in human beings. The attitude of submission to authority other than the authority of facts and rationality is demoralising for scientific temper. By its very nature scientific spirit is anti-authoritarian and it tends to dethrone every idol however high its source or sanction may be. To remain immune to the corroding influence of the authoritarian society, the Indian scientists have to offer stubborn resistance to age-long authority firmly entrenched at different ideological planes.

(d) *Social Vice—Hypocrisy*: Basically, scientific research is a quest for truth and for its proper functioning an environment of truth is essential. In a society where hypocrisy is rampant in all strata, the climate of research is bound to be adversely affected. Hypocrisy brings about a split in the conduct of the individual and for a scientist it will have damaging consequences. It results in difficulty of communication and ends up with crisis in confidence. Lack of confidence in indigeneous know-how, lack of faith in our ability to build and manage and craze for foreign experts, etc. are due to prevalence of hypocrisy in our social life.

(e) *Philosophy of Life*: In India, philosophy of life is essentially based on spiritual ideals which have a long

tradition. Spiritual philosophy provides answers to the ultimate problems of human existence. The philosophy of science on the other hand has no answer to offer regarding the eternal problems of human life, the reason being that science is not perfect as it is a product of human beings who are themselves imperfect. To a logical and discerning mind the two sets of ideals cannot easily be reconciled, nor is it possible to divorce them in the day-to-day life of a scientist. This has interesting consequences on the conduct of scientists. This divided loyalty to two sets of ideals is responsible for lack of passionate zeal for science as there is gradual erosion of the faith in the philosophy of science. As scientists grow in age they are caught in the vortex of prevailing ideologies in the society and it is not an uncommon phenomenon to see a scientist put on a talisman or to consult astrologers, etc. A sort of fatalism gets the upper hand and slowly scientific spirit is replaced by traditional thinking. The belief that it lies within our power to change the surroundings to our advantage and that science offers such an opportunity provided that we have confidence in the method of science is essential for the growth and development of science. We, the scientists in India, have to become conscious of the environmental factors which directly or indirectly affect the growth and development of science and suggest ways and means to ensure proper interaction between science and society with proper feedback so that society flourishes along with science by synergetic effect.

Fertilizer Industry Round Table 1969*

At the 19th annual meeting Fertilizer Industry Round Table held in Washington during Nov. 5-7, 1969 various aspects of fertilizer industry were discussed. Hugh S. Ten Eyck in his keynote address, entitled., Whither Away Fertilizers, discussed the basic technical and production data that appear to be in the offing. In the USA there is a tendency towards production of the most concentrated fertilizers, the conversion within the market area of these concentrated products to finished goods and their distribution, an intensification of the production of high analysis finished goods which will provide increased agronomic yields/dollar requiring new farming techniques and the intensification of basic concentrated raw material manufacture in those areas. It appears that the potassium salts used as fertilizer will stay long today for supplying K_2O in the economical form. Nitrogen as ammonia has reached its maximum concentration with the availability of cheap gas, and with the advent of big ammonia plants in Maracaibo area, the Arabian Gulf and North Africa the future of the producers in other areas become shaky. Phosphoric fertilizers in the form of triple superphosphate and concentrated ammonium phosphates are now appearing. With the availability of cheap atomic power located at phosphate rock mines elemental phosphorus can be competitive in the world of phosphatic products.

LE Boswik and William Turner discussed Edwin Lopker's contribution to the technology of phosphoric acid manufacture by the invention of a new process in which phosphate rock rapidly and completely reacts with sulphuric acid and the resultant calcium sulphate crystals grow rapidly to such a size and shape that separation of the phosphoric acid from them is more rapid and complete than with any other process. With this process, a full-scale plant is giving satisfactory production result. The operation of Kellog-Lopker system has been described. The overall conception of the process is that if the calcium sulphate is crystallizing well, the whole system is functioning smoothly. Phosphate rock and the recycling phosphoric acid solution from the filter system are fed into the dissolver and swirling action is adequate to mix them into the recirculating slurry. In the evaporator the sulphuric acid is distributed over the surface of the swirling slurry and mixes with it. The process differs from others; in that the changes in calcium and sulphate ions concentrations are very small, controllable and predictable, and most of them are separated in time as well as in space. In the Kellog-Lopker system there is reduced capital investment/ton of P_2O_5 produced. The overall reduction in manufacturing usually amounts to about 30 per cent equivalent to a cost reduction of well over two dollars per ton of P_2O_5. The existing plants can be easily and economically converted to the concepts of the process.

Richard. M. Daniel discussed hemihydrate-dihydrate process for manufacturing phosphoric acid which in Japan is widely accepted because of better short and long term savings and reliability of this process in giving consistent savings over a long period of time. In the wet process phosphoric acid, the degraded quality of standard gypsum, obtained as a by-product, is either unacceptable to the consumer or non-competitive. The greatest obstacle to the development of uses of chemical gypsum is the almost complete lack of ties between the gypsum and fertilizer industries. There is also the problem of disposal by-product gypsum, for making this product usable, a proceedure of considerable interest is the Ginlini process which was developed in W. Germany. A plant has been built which recrystallizes waste chemical

* Proceedings of the 19th Annual Meeting of Fertilizer Industry Round Table 1969, held at Washington.

gypsum to produce 165 tons/day of either hemihydrate powder or building blocks with production cost of £4.10/ton. In this process there is formation of alpha crystals of hymihydrate rather than beta from which results calcination.

Fluid-bed drying systems are receiving more attention for all types of drying applications. R. J. Priestley and D. W. Leyshov discussed fluid beds for phosphates. They reviewed in their paper the basic characteristics of fluidized-bed drying and calcining of phosphate rock and features of these systems in their most advanced form. Two very recent phosphate rock processing developments are: (i) beneficiation by fluidized-bed sizing in a drying system, and (ii) calcination for calcium removal. Additional applications to the fertilizer industry, now under development, are suggested. The basic requirements of the accepted practice of fluidized-bed built in the USA are fuel and space efficiency, simple and flexible operation and low cost. Recent development of fluidized-bed with sizing and lime removal has been described.

J. J. Boyce and J. R. Carney read a paper on compaction-granulation of fertilizer materials. Compaction is the agglomeration of finely divided materials into a dense, continuous sheet. Granulation is the subsequent size reduction operation. The raw materials are blended or mixed in the proper proportions for a specific NPK content. Here the smaller the particle size of the raw materials, the more homogeneous the final mixture. The mixture is then compacted into a sheet followed by grinding or granulation and screening to separate out the desired final particle size. Compaction and granulation can produce a granulator product from single materials, such as urea, MAP, DAP and others or mixed and complete fertilizers in whatever combinations, are desired. Some compacters and compaction granulation system and the capital and operating costs for compaction and granulation of fertilizers have been discussed.

A hardness test conforming to standard of granular materials of fertilizers has been described by Charles Dirdak of the American Potash Chem. Corpr. The hardness of fertilizer particles is important because of degradation and dusting as the material is handled. The significance of variables determining the hardness in order to help users select appropriate adjustments to the procedure that make it suitable for a great variety of products. The precision of the procedure is expressed in terms of standard deviation of breakage index.

Air and water pollution problems due to fertilizer industries have been dealt with. The annual damage in USA air pollution does to crops, buildings, equipment and other property is estimated at £11 billion, without even calculating the health hazards, pollutants such as sulphur dioxide and suspended particulates can aggravated asthma and other chronic respiratory diseases and in large enough concentrations can even cause death. In USA a number of states have established air pollution control boards, air quality boards, subsections of their public health departments, charged with the problem of pollution control. Controversies are there on pollution and how to control it. Edwin Cox in his paper discussed the water pollution regulations and tolerances as they apply to fertilizer industry. Fertilizer usage may be regulated because of its effect on water pollution and for regulations involving expenses. Examples of stream classification and stream quality have been dealt with.

James P. Tomany read a paper entitled 'A Guide to the Selection of Air Pollution Control Equipment'. Air pollution contract is concerned with the removal of gases, vapours and particulate matter, either separately or in various combinations from process exhaust streams. Such emissions as solvents from drying ovens, nitric oxide gases from chemical processing plants, fly ash and SO_2 from power plants, ammonia and phosphate dusts from fertilizer operations represent some of the problems encountered in the air pollution control field. Equipment made for the solution of these various air pollution problems. The three equipment types available for the control of gases of vapours are combustion, adsorption and absorbtion devices. The four major types of equipment utilized for the collection of particulate matter are mechanical collector, electrostatic precipitator, fabric-filter and wet scrubbers; these have been described. The aspects and costs of air pollution control within the phosphate fertilizer industry were discussed by Lawrence J. Hill. Rock drying, defluorination of phosphate rock, calcination of the rock all involve pollution problems. In the thermal and wet processes of phosphoric acid, normal superphosphate, triple superphosphate and ammonium phosphates and NPK fertilizers manufacture various pollution problems have been come across and how these are tackled involving costs have been dealt with.

The formulation is the process by which raw materials which constitute 80 per cent of the manufacturing cost of the fertilizer are selected and used in granulation. Jon L. Nevins and Frank P. Achorn read a paper entitled 'Formulation for a TVA-type Ammoniator Granulator by Computer'. With so many technical and economic factors to be considered, the computer has been resorted to as a means of calculating granulating formulation and solutions are given with the help of linear programming models and operational research. John T. Hailey and

R. H. Perkins also discussed formulations. Perkins said that the following have proven of benefit in establishing a high degree of flexibility in formulation within their plants over the years. (1) Frequent studies are made of prevailing raw material costs by geographical area and their formulations are re-evaluated in light of any significant raw material cost changes. (2) Plant tests are made frequently to determine if new combinations of materials offering greater economy can be utilized. Detailed information as to how the test should be made must be supplied the plant and a careful review of results of each plant trial is essential. (3) Plants should be provided with equipment suitable for handling and processing a wide selection of raw materials in order to take greatest advantage of formulation benefits. Some examples of formulation and process development in the plants have been given by the author.

Robert R. Heck discussed in his paper the gross heat effect in the granulation of NPK fertilizers. In attempting to increase tonnage of fertilizer production effects of small increase are first tested say from 20 to 22 tph. When this was successful, then another small increase was tried—say from 22 to 25 tph. These tests are made on the assumption that incremental increases will measure the success without creating problems such as the build-up of excessive recycle or excessive over-agglomeration. In order to better understand the conditions under which the plants could be operated, a series of tests were conducted to measure the effect of throughput increases on granulation characteristics.

In an attempt to determine the differences between the plants, an analysis was made of three variables that existed in ammoniator-granulator drums of the different plants i.e. bed volume, bed surface and heat-loss area. Establishing the limiting factors of these three variables, they were applied to other ammoniating drums. Based upon guess estimates, the effects of three factors on production rates were found. Using the calculated maximum heat and release, the maximum production rate was calculated. Based upon previous assumptions and realization of the predicted tonnage rates, another application for the ammoniator heat parameter, i.e. determining production rate of low-heat formulae to attain optimum granulation, was made.

Shrinkage in fertilizer plants was discussed by John. L.Rogers and a statistical approach to shrinkage measurement was outlined. The objective of this programme was and is to correlate shrink data from several granulation plants in such a manner as to be able to compare the performances of individual plants and, of even more importance, to be able to place proper emphasis on reducing losses of fertilizer materials. The success of the programme depends on gaining a knowledge of the true operational experiences of the plants involved and this, in turn, requires that measuring bases must be uniform according to established definitions (given below).

Number One: Shrink is the difference between the materials received in a plant and the materials removed from the plant, including the change in internal inventory.

Number Two: Materials bought and materials sold are N, P_2O_5 and K_2O. Shrinkage is measured in terms of unit-tons of these plant foods.

Number Three: The total measure of materials in and out of a plant during a specified time period constitutes the material balance. A nominal material balance is based on grade numbers of materials shipped and nominal analyses of raw materials received. An actual material balance is based on the true chemical analysis of raw materials, inventories and products.

Number Four: Economic loss is the loss of N, P_2O_5 and K_2O due to the difference between the actual quantities of raw materials available for use less the nominal quantity shipped as grade numbers during the same time period.

Most nitrogen is lost as ammonia from granulation stacks. A quantitative test method was applied to assess this loss. Losses in ammoniation stacks were found out. Many factors are responsible for excessive shrinkage and each plant requires searching studies to eliminate costly shrinkage and for this some suggestions have been offered.

The lack of uniformity of the fertilizer products from the granulator is reflected throughout the entire granulation system, as well as in the finished product. As a solution of this problem a granulation process has been developed designated as the C.B. Granulation process covered by Canadian and U.S. patents. The process has been described by James E. Madigan and Cam Bolduc in the paper entitled 'C.B Granulation Process'. A high degree of uniformity of products has been demonstrated by following this process.

Robert W. Clark read a paper entitled 'Low Fluorine Triple Superphosphate'. In the face of phosphate industry expansion the producers have been confronted with ever tightening restrictions on air pollutants because of the presence of significant quantity of fluorine in rock phosphate. So the gases are either scrubbed when vented from the huge curing sheds or adopt some alternate process which would not occasion fluoride emissions. A new approach to this problem has been offered by Reynolds, Smith and Hills in which by increasing the

fluorine evolution during the acidulation step where thee gases could be more easily scrubbed and thereby reduce the fluorine content of the product to a level where additional fluorine would not be evolved during curing the storage. The essential feature of the process is the use of hot phosphate rock along with hot acid, followed by denning, cooling, crushing and screening of the product. A series of bench-scale tests and pilot plant runs have been made to develop and evaluate this process. Some work was done using nitric and hydrochloric acids which demonstrated the processes' applicability using these reactants. However, the majority of the work has been done with sulphuric and phosphoric acids and it is this work that has been discussed here.

The basic work has included investigations on various acid supplies, various rock supplies, ranges of acid and rock temperatures, ratios of acid to rock, additives, and varying time and temperatures of denning.

The bench-scale work was carried out using a kitchen-mixer with stainless steel bowls for the acidulation step. The acid was heated on a hot plate while the rock was heated in aluminium foil boats in a muffle furnace. This method assured that the rock was at a uniform temperature. The bowl was preheated to reaction temperature. In an oven, the hot acid was dumped into the bowl and the hot rock added during mixing, taking about 10 seconds to complete rock addition. Mixing was then continued until the product had begun to "set up" at which time the bowl was dumped and the material broken up with a spatula. The crushed product was then immediately transferred to a beaker and placed in an oven for denning at a specified temperature and time interval, after which the beaker was removed, lightly covered and allowed to cool to room temperature. Analyses were performed after twenty-four hours. Standard AOAC analysis methods were used throughout.

The hot rock-hot acid process utilizes phosphate rock heated to 250 degrees F and up and wet process phosphate rock heated to 250 degrees F and up and wet process phosphoric acid heated to about 250 degrees F to produce a semigranular triple superphosphate which does not evolve significant quantities of fluorine during curing or storage. The process will cost from £ 0.40 to 0.75 per ton above current cost. Credit for by-product fluosilicic acid can convert this to a \$ 0.30 to \$ 0.60 per ton savings. Even without such credit, the process offers a lower cost alternate to installation of scrubber complexes on curing buildings.

For those plants using very low grade acid with high fluorine contents, it may be necessary to add some silica to achieve the desired fluorine evolution. This cost, however, can be offset by the by-product fluosilicic acid produced.

In addition, there are other benefits to which it is difficult to affix dollar values, such as essentially eliminating a dust problem, increased loading rates and improved working conditions due to reduced fluorine in the air.

Work on this process was begun by Mr. Albert Henderson in 1962. Reynolds, Smith and Hills became involved in 1967 providing engineering evaluation and design services. A patent application was filed in December 1967. The pilot plant was constructed in early 1968, and work has been continuous through this period and is still continuing.

(B. K. BANERJEE)

Fertilizer Statistics 1969-70 (Fertilizer Association of India, New Delhi), pp. 656 including 16 illustrations, Price Rs. 25/-.

In view of the growing demand for fertilizers the study of production and application of fertilizer is assuming more and more importance. Those engaged in fertilizer study would like to know the relevant information regarding the various aspects of fertilizer industry, like raw materials position, installed capacity, actual production, prices of fertilizer, production of various crops in the country etc. Such type of data connected with fertilizers is available on piece-meal basis in a very few journals and also found in records of Government and industry mostly unpublished. The Fertilizer Association of India is doing commendable service in bringing together all this data at one place in the form of a book every year. The present book is fifteenth in the series since 1956. This edition brings up-to-date statistical data furnished in the previous editions.

The book under review is divided into three main parts, viz. Fertilizer Statistics, Agricultural Statistics, Selected World Fertilizer and Agricultural Statistics. The first part comprises of tables containing nitrogenous, phosphatic, potassic and mixed fertilizers, production-consumption targets in Fourth Five Year Plan, and miscellaneous statistics like fertilizer recommendation for crops, guide for mixing fertilizers, list of soil testing laboratories, etc. The second part deals with classification, area, production and average yield per hectare of principal crops (all-India and statewise), seasons and crops, population and agricultural economy, target of agricultural production in the Third and Fourth five year plans. The third part consists of world fertilizer and agricultural statistics.

The book covers all sorts of statistical information needed by a worker in the fertilizer study and is most useful to industralists, planners and engineers alike.

[S. A. KULKARNI]

1970 Paint Red Book.—Edited by L. Sheckman (Palmerton Publishing Co., New York 10001) pp., 416, Price U.S. £ 15.00

The third edition of the Paint Red Book, the directory of the coatings industry, is now available for general distribution. This highly important and interesting book offers complete listings of all paint and coating manufacturers in the United States and Canada and complete listings of formulated paint and coating products. Listings are furnished for all types of raw materials, production, application and aerosol equipment, testing services, and consulting laboratories. A 'Who's Who' section provides an alphabetical list of all pertinent people in the paint and coatings industry. Included also is the detailed alphabetical subject index to the volume. The following contents are of great interest: Manufacturers of formulated paint and coatings, formulated paint and coating products, formulated paint and coating plants in the USA, suppliers to the paint and coatings industry, machinery and equipment, raw materials, additives, driers, drying oils, extenders, intermediates, latex emulsions, pigments, plasticizers, resins, rust inhibitive pigments, solvents and aerosol raw materials, consultants and testing laboratories, trade associations, Who's Who, and advertising index.

The reviewer has seen several publications in this direction and feels that the 1970 Paint Red Book is the only complete, if not absolutely, directory in the field. This excellent compilation will be highly usuful for users as a guide for all raw materials, machinery and equipment and services offered to the industry. The reviewer strongly recommends this valuable publication for everyone interested in paint and coatings and especially every library in India.

[VIJAY MOHAN BHATNAGAR,
Cornwall, Ontario, Canada]

Flameproofing, Bibliographic Series No. 185 by C. J. West, E. Stringham, L. Roth and J. Weiner, pp., 224 *Supplement to No. 185* by J. Weiner and J. Byrne., pp., 121 Price \$ 20 and \$ 16 respectively. Published by The Institute of Paper Chemistry, Appleton, Wisconsin, U.S.A.

In the USA, some 12,00 people were killed in fire and there was \$ 27,00,000 loss in property. In Canada, there were 624 fire deaths, over one-third of them being children. Most of the roughly 65,000 fires reported were in residential property and caused a loss of about \$ 200 million. These figures are for 1969 as complete figures for 1970 have not yet been compiled. Such fire losses can be cut to a great degree by using fire-retardant materials or flameproofing agents. The word fire retardant usually implies paints or coatings materials that will slow down, impede the progress of fire. The term generally refers to a coating system that will not only prevent the progression of fire but also insulate and protect from heat the base to which the coating is applied.

The flammability behaviour of many materials have recently been receiving considerable scientific attention. The increasing number of publications in various journals, the frequency of references at various scientific meetings and the increasing number of symposia on the topic are a testimony to this active technical participation. The *American Paint Redbook*, 1970 shows that nearly 380 American and Canadian chemical companies are now engaged in fire-retardant work. As more synthetic material is being used in the building and automotive industry as well as in various personal and household products, the flammability of these objects was/will become a real concern. As in the USA, and Canada, India will definitely need State and other fire codes which will specify use of fire-retardants in houses, hotels, motels, cinema houses, government and public buildings. The Indian chemical industry will have to do something about developing fire-retardants and their application. Several consultants—foreign, Indian, etc—could help the government and the industry in such an important field. Concerning USA, and Canada, the size of the market, viz. over 100 million pounds of flame-retardant sold in 1966, is an indication to this participation. The amount goes in billions, upto 1975.

The first book is divided into 9 broad subjects: paper, board, wood, textiles, plastics, coatings, testing, synthesis, and general. There are in total 876 abstracts with author, subject and patent indices including two patents from India—patent nos. 53, 493 and 53,399/November 7, 1956, both dealing with flameproofing of textiles. A general discussion on flameproofing is incorporated into the introduction. This introductory discussion is like a summary of flameproofing theories, techniques, and agents included to acquaint the readers with the general aspects of

flameproofing. Supplement 1 to No. 185 is divided same as in No. 185 series.

In view of the increasing interest being shown in flame retardants, there is a definite need for such books. The two books are undoubtedly important contributions to flameproofing field and can be strongly recommended to every Indian science library, and individual interested in flameproofing.

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Agronomical Studies on the Relative Efficiencies of Citrate and Water-soluble Straight and Complex Phosphatic Fertilizers under the Agroclimatic Conditions of Eastern India, by Dr. S. P. Dhua, TECHNOLOGY, Vol. 7, No. 3, 1970 (Special Issue). Price Inland: Rs. 8.00—Postage Extra; Foreign: $ 2.50 (inclusive of sea-mail charge)—air-mail postage extra.

The two principal ways of raising agricultural production are by expanding the area cultivated and by improving crop yields and animal production by adopting modern methods. Under the present condition of population explosion and increased urbanization of village areas, it is rather difficult to make any notable expansion of the area cultivated and the second method of raising agricultural production, therefore, appears to be feasible. The two principal requirements for improving yields can be met if under improved irrigation, crop protection and modern farm equipment facilities, quality seeds of high-yielding varieties are grown in presence of innocuous fertilizers.

Since time immemorial, it has been known that lands improve in their crop-producing capacity provided certain extraneous matters are added to them. Liebig's mineral theory (1840) and his emphasis (1856) on the necessity of providing plants with phosphorus and potassium followed by the discovery by essential nature of nitrogen by Lawes, Gilbert and Pugh (1857) gave the first scientific footing to the use of such extraneous matters in the form of what we now call 'fertilizers.' Liebig's (1839) demonstration on the increased fertilizing value of bones with the treatment of sulphuric and hydrochloric acids and similarly of ground phosphate rocks with such treatments (Lawes, 1842) gave the production of the most popular single fertilizer that the markets in any part of the world have ever seen, viz. superphosphate (Lawes, 1843). Ammonium sulphate—another popular fertilizer—probably came in the market some time in 1893. Subsequently, the world has seen the production of varieties of fertilizers every time the esentiality of a new element is recognized.

Gradually, it is, however, thought that to lower down the unit cost of any fertilizer with respect to certain nutrient elements, high analysis and more complex fertilizers should be developed according to the area cultivated. Nitrogen and phosphorus bing the two most important nutrient elements, efforts were made to combine the properties of the two popular fertilizers representing them, viz. ammonium sulphate and superphosphate. In the beginning of the twentieth century, voices were raised about the residual acidity of superphosphate and since phosphate is thought to be the bottleneck of world's hunger, techniques were developed to neutralize this residual acidity of superphosphate. In the mean time, acute sulphur deficiency in the world necessitated the use of easily available nitric acid (or hydrochloric acid) for the manufacture of superphosphate from rock phosphate. The ammoniation of this superphosphate in 1930 is thought to be one of the most significant developments in the fertilizer industry as this enabled the farmer to use cheap forms of fixed atmospheric nitrogen.

Indian soils generally lack in nitrogen and phosphorus and efforts made toward the improvement of these two important nutrients in these soils especially to increase output of the important crops of India, such as paddy, wheat, sugarcane and potato, should therefore be appreciated. This is more so under conditions of availability of a variety of nitrogenous and phosphatic fertilizers which makes it rather impossible for the farmers to select the proper fertilizers for their lands.

The efforts that are being made by the agronomists, headed by Dr. S. P. Dhua, of the Planning & Development Division of the Fertilizer Corporation of India towards easing this situation are well reflected in this special issue of TECHNOLOGY. The publication incorporates the results obtained from pot culture and field experiments to evaluate the relative efficiencies of citrate- and water-soluble forms of phosphorus given in the form of straight (superphosphate, multiphosphate, calcined phosphate, fused phosphate and rock phosphate) and complex fertilizers (ammonium phosphate, ammonium phosphate sulphate, carbonitric nitrophosphate, sulpho-nitric nitrophosphate and *suphala*) in the five states of eastern India, viz. West Bengal, U.P., Bihar Orissa and Assam. The experiments were carried out for a number of years to neutralize the effect of seasonal factors and under acid, neutral and alkaline conditions of soils to avoid the effects of soil variations also. Improved varieties including some local varieties of the crops, viz. paddy, wheat, potato, maize, jute, sugarcane and groundnut, were taken as test crops. Uptake of

citrate- and water-soluble phosphates from different grades of nitrophosphates prepared in the laboratory tagged with radioactive P^{32} was studied by pot culture experiments both from the point of view of quality and quantity of uptake by the test crops at their different physiological stages. In view of the large number of experiments done and the nature of the statistical analyses of the results observed, the repeatability of the results are definitely assured under such variable factors as season, soil, crop and management. The two outstanding conclusions that have been made from such experiments are that the crops at their early stages of growth respond better to the water-soluble forms of phosphorus up to a limit of 25-30 per cent, the superior effect of which is not conspicuous as the crops reach the threshold of developmental stages when citrate- and water-soluble forms of phosphorus appear to be equally effective and that nitrophosphates with 25-30 per cent water-soluble phosphorus and 50 per cent ammoniacal nitrogen and 50 per cent nitrate nitrogen prove to be the best fertilizers at least for the seven crops mentioned earlier and under the agroclimatic conditions of eastern India. Such products may be manufactured in India without hammering much upon the sulphur reserve of the country provided ODDA or sulphate recycle process, which is claimed to be economic under Indian conditions, is followed.

Prior to this work, no such systematic attempt was made particularly in India to evaluate the citrate- and water-soluble varieties of phosphatic sources especially nitrophosphates under such a variety of conditions and with such a large number of experiments. The soils of the eastern parts of India because of heavy rainfall generally lose much of their fertility especially with respect to nitrogen, calcium and phosphorus and therefore, the entry of these nitrophos fertilizers containing all these three elements is welcome. It is indeed heartening to note that to a very great extent these fertilizers are innocuous.

The author has very nicely dealt with the subject-matter of these fertilizers in seven chapters with ample figures and tables and with the observations made by other workers in the line. The publication shows the experience of the author and his erudition on the subject.

It is, however, felt that in the larger interest of the subject, the inclusion of some photographs depicting the relative efficiencies of the fertilizers and the economics of these fertilizers, showing clearly the profit in terms of rupees for every rupee spent for the purchase and application of the fertilizers, would have added value for the publication. It is hoped that the nitrophosphates used were free of fluorine and rarer elements otherwise their residual effects seen on the subsequent crops might not be reliable and might endanger human lives with such diseases as fluorosis. It is not to be forgotten that we have a very weak extension department and our farmers are yet to be made conscious about the utility and object of fertilizer use.

Nevertheless, the publication is a very good addition to the literature on fertilizer chemistry and should find a place in every agricultural library.

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Notes & News

Sea Water for Irrigation

Nearly 36 per cent of the gross land area of the world lies in the arid to semi-arid region where the rainfall is too scanty and erratic to support plant growth. In such area the water available is brackish and the plant growth is restricted to some drought or salt-tolerant species. Recently many countries have investigated the possibilities of bringing under cultivation the sand dunes with saline water. In Israel, a part of the desert was converted to an evergreen garden with trees, shrubs and ornamental plants using underground water having 2000 mg./1 salt. Later, more than 200 species of plants were introduced by irrigating with the Mediterranean sea water having a salinity range from 1000 mg./l. to oceanic concentration and on experimental basis vegetables, forage crops and plants for industrial use were successfully grown by irrigating with Caspian sea water. In Sweden, grasses and legumes were grown by irrigating with Baltic sea-water (6 g/l.). It was found that on clayey soil the yield decreased to 55 per cent while on sandy soils over 60 per cent increase was observed. The water from the North Sea containing 32 g/l. of salt resulted in the luxuiriant growth of *Agropyrum Junceum* in W. Germany. At the Marine Agricultural Station in Spain, attempts were made to grow many food, forage and vegetable crops by sea-water irrigation. Large scale cotton cultivation with saline ground water on coastal regions has been achieved in USSR.

India has great potentialities for harnessing sea-water and vast coastal sandy belts estimated at 8.5 mil. hectares along the 5600 km coastline. The Central Salt and Marine Chemicals Research Institute, Bhavnagar has since 1963 undertaken evaluation of sea-water tolerance of crop plants which can be cultivated on coastal sandy belt taking advantage of regional rainfall and low sea-water salinity. Laboratory experiments were carried out with many varieties of cereals, pulses, oilseeds millets and forage crops to screen at germination and early seedling stage usings sea-water of different salinity grades. Among the various crops studied, *bajra* (Babapuri) sesamum (TMVI), groundnut (Punjab 1), linseed (RR 9), mustard (local), safflower (NP 30), wheat (*Karchia* and *Kata*) and alfalfa (local) were highly tolerant to sea water during the gergmination stage. Very low dilution of sea water stimulated the plumule and radicle growth but 10,000 ppm sea water or above reduced it more or less in proportion to the increase in the salt content of the media.

Metabolic studies conducted with seedling of wheat, barley and Bengal gram under controlled conditions revealed that the amendment of sea-water dilutions with Hoagland's nutrient overcomes considerably the depression of general metaboic rate. Respiratory activity was reduced by sea-water application, and amendment with nutrient salts stimulated the endogenous respiration in root portions. The phosphorus metabolism of wheat, Bengal gram, safflower and *bajra* seedlings under saline conditions was investigated with radioactive phosphorus (p^{32}) and it was observed that salinity did not inhibit completely the uptake of phosphorus, but translocation and incorporation of absorbed phosphorus from inorganic to organic compounds was reduced using radioactive chlorine it was found that the antagonistics effects were produced by the added salts, specially calcium nitrate and potassium dihydrogen orthophosphate in seedlings grown with sea- water dilutions. Protein synthesis was affected by sea-water treatment by an increase in the soluble protein. The monocot and dicot responded differently to salinity treatments.

The sea water tolerant varieties of wheat, barley, *bajra* and safflower seeds evaluated at germination stage were further tested in pot cultures, with a view to assessing the limit of sea water tolerance at vegetative and reproductive phases of growth and also yield characters. The acclimatization of crops with gradual increase in sea water salinity was made for a period of 3-4 years with sea-water dilutions and amendments with various nutritive salts. *Bajra* (*Babapuri*) which was not sea water tolerant earlier, was acclimatized to direct irrigation with sea-water within 4 years. For wheat, barley and safflower the maximum limite of sea water tolerance was only 20,000 ppm of sea water even after acclimatization.

To determine the exact fertilizer requirement of crops under field conditions, sand bed cultivation of acclimatized seeds of wheat (*Karchia* and NP 824), safflower (NP-30) and *bajra* was carried out following the pot culture experiments. Water-soluble and commercially available fertilizers were applied at the required dose. In general, the crops responded well to sea-water irrigation from 40 days onwards to maturity. The vegetative growth of plants was quite satisfactory and salinity effects were not exhibited by plants. The grain yield was reduced to 30-40 per cent as compared with the yield obtained employing fresh water irrigation. Field experiments with acclimatized seeds of *Bajra* are in progress. Two field experimental stations are being established—one at Hathab near Bhavnagar and the other at Pondicherry.

The investigations carried out so far indicate the possibilities of growing acclimatized seeds of highly tolerant varieties of crops on sandy belt by sowing in the rainy season; the growth of plant can be acclerated by fertilizing them initially and during non-rainly season sea water can be accelerated by fertilizing them initially and during non-rainy season sea water can be effectively utilized for irrigation purposes.

[*CSIR News*, **20** (21) (1970), 164]

From Laboratory Research to Industrial Application

A seminar on problems of transition from laboratory research to industrial application, organized jointly by Unesco and the Government of India, was held at the National Chemical Laboratory (NCL), Poona during 9-14 December 1970. Thirty-two scientists from 14 Asian and other countries participated in the seminar,

which was inaugurated by Dr. Atma Ram, Director-General, SIR. Dr. B. Oberbacher (Batelle Institute, Frankfurt, West Germany), Dr E. S. Stanley (Arthur D. Little, Inc., Cambridge, Mass., USA), and Dr. B. D. Tilak (National Chemical Laboratory, Poona) acted as the directors of the seminar.

21 papers formed the background material for exhaustive discussions in three sessions. The following topics were extensively discussed in two panels: prerequisites to successful industrial research; rationale of technology development and the transition of laboratory research to industry; and transition of laboratory/pilot plant research/development to industry.

In his inaugural address, Dr. Atma Ram said that development should be a major responsibility of the industry and not mainly of the research laboratory. The laboratory's role should be that of the 'idea producer'. He was happy that greater attention was being paid to project and consulting engineers and that sponsored research was being encouraged. In the case of NCL, this policy had already started paying off. He stressed the need for judicious selection and proper management to to see the project through.

In his welcome address, Dr. B. D. Tilak observed that on account of sheltered markets and the Government's protective policies, indigenous research and development was lacking. Industrial utilization of laboratory technology was beset with many problems even in advanced countries, and in developing countries difficulties were formidable. To overcome the Indian scientist's inability to demonstrate the operation of a full scale plant based on his know-how, Dr. Tilak observed that emphasis should be placed on associating project engineers in an increasing measure, or alternatively industry should build up its own development wing.

Dr. V. P. Kahr, Deputy Director, Field Science Office for South Asia, Unesco, New Delhi, outlined the purpose of the seminar in identifying the difficulties encountered, the efforts made and the possible solution to be found to the problem of transferring the results of scientific and applied research to industry and economic utilization. He expressed the hope that the deliberations would be fruitful to the participants, the member states and Unesco for further international coordination and understanding.

Recommendations: (1) For strong economic growth in the developing countries, the need for adequate R and D base was stressed. In those countries where most of the R and D inputs are by the government, the seminar recommended that funding of R and D by the government could be used as a tool for promoting the economic growth according to the identified priorities of socio-economic needs.

(2) In view of the imbalances in the availability of trained laboratory researchers, engineers, technicians, technologists, technocrats/managers in most of the participating countries, it was recommended that the overall training of manpower should be coupled with the plans of social and economic growth by a planned process of education. This could be done by the respective governments by adequate funding in the desired direction. The importance of management training for scientists of all senior cadres in R and D institutions was stressed.

(3) The need for intimate relationship between scientific and technical institutions, universities, R and D institutions and government was stressed.

(4) For improving the efficacy of R and D institutions in developing countries in the proper identification of projects, it was recognized that collection and dissemination of local and international market information is of great necessity. This can be arranged by establishing market information exchange centres in different countries. Since there are no such centres in South Asia, international assistance may be secured for providing expertise in market research methodology and in establishing such agencies.

(5) Observing that a high order impact on the economic growth of the developing countries can be effected by adapting, assimiliating and improving upon imported technologies, the seminar recommended the following measures: (i) Large industries in the developing countries should be encouraged to establish integrated R and D and engineering and design facilities which will facilitate the expansion of these units on the basis of their own 'inhouse' research. Government may subsidize such inhouse research by affording adequate incentives. (ii) Until such R and D base is established, the large industries in these countries should take advantage of the national laboratories. This can be accomplished, for example, by funding sponsored research on the problems connected with the assimilation and improvement of imported technology as well as problems of diversification and expansion. Government should give such a directive to all public sector companies that they formulate definite and time-targeted plans for absorbing and improving imported technologies. (iii) The government should also promote industries in key sectors by funding research on important problems in research establishments in public and private sector industries and in other R and D institutions.

(6) The seminar felt that it would be mutually advantageous to establish bilateral collaborations in R and D activities between different South Asian countries. This may be effected by the following ways: (i) exchange of scientists among developing nations as the first order priority; (ii) strengthening of the UNIDO journal, which records technological progress, in the developing nations; and (iii) sponsoring of research and development work across national lines to take advantage of the available expertise and facilities in other countries. Apart from the desirability of establishment of international market information centres as mentioned earlier, it was recommended that such centres may serve as an agency for exchange of technological information among R and D institutions in the respective countries. This could be done through exchange of annual reports and other relevant publications of the institutions.

(7) Most of the representatives felt that it was important to be selective in R and D inputs in view of the limited resources. They recommended that it was necessary to have a well-defined national scientific and technological policy to promote indigenous research in selected fields of highest relevance. The government should also have a policy of implementation of such plans by making available necessary funds.

(8) For successful horizontal transfer of technology from laboratory research to industry, the seminar considered several factors such as the need for associating the prospective user at an early stage; project engineers for large projects; and of financial institutions which can provide risk capital. Since exclusivity of licensing may be difficult, the practical recourse is the provision of adequate lead time to the prospective pioneers. The need for providing financial guarantees of the performance by R and D institutions was also recognized. Encouragement of sponsored research was emphasized as it is most likely to lead to the success of transfer of technology. Scientists and technologists were exhorted to strive to

bridge the communication gap existing between them and the business entrepreneurs.

(9) An important factor for horizontal transfer of technology is the establishment of effective public relations of publishing success stories of technological development and research work accomplished by R and D institutions.

Miscellaneous: The seminar also discussed the factors which promote vertical transfer of technology within an organization. These included: clear definition of objective; acceptance of the objectives by the top management, and acceptance and and communication of the objectives throughout the research, development, production and marketing organizations; and encouragement of R and D scientists to work in production units, marketing or other departments in the organization. For achieving success in large and difficult projects a total systems approach was found essential. This would involve the constitution of a team from various disciplines and expertise in the technology transfer chain.

The seminar also laid stress on the need for purposeful management of research agencies and institutions.

[*CSIR News*, **21** (2) (1971), 1]

Soviet Agriculture

Since November 1969, the kolkhozes or collective farms have a new constitution which is development over the previous constitution promulgated in 1935. The draft model was approved with some additions and amendments at the congress of kolkhozes held in early November 1969.

The kolkhoz in the Gus Khrustalny district of Vladimir province was founded in 1928, which consisted of 7 families living in a communal tent and were given 16 hectares of land. With time it expanded and now covers 14,000 hectares including 13 villages with 550 families. Its members now live in 3- or 4- roomed cottages, each accommodating one family.

The five years following the second world war marked a turning point in kolkhoz history in 2 ways, one involuntary, the other due to governmental decision. The first was a general agricultural decline (up to 1951) due to war losses and to a switch to industry, for many of those demobilized did not return to their rural areas, and also deterioration in the means of production. The second factor was the decision taken in 1950 to combine small kolkhozes into large units and some 254,000 small kolkhozes were amalgamated into 124,000 farms by that year and today the same stands only at 36,000. According to 1964 statistics only 15 per cent of kolkhozes consisted of a single village, whereas 35 per cent comprised more than five localities; it has become difficult to convene a general assembly.

In March 1956 the Government decided to strengthen the relations between kolkhozes and the machine and tractor stations in developing kolkhozes collective economy and since then supervision of the latter has been vested in the local administrative agencies of the State and the Party. The disappearance of nearly 20 million people from the collective farm population is due to (a) migration to town and (b) transformation of many kolkhozes into state farms (sorkhozes). Between 1929 and 1967 the rural population in USSR increased by 18 per cent, but it represents 45 per cent of the total population and stands at the same figure of 106 million as in 1879. It may be generalized in the following way: between 1939 and 1967 the rural population in Soviet Central Asia increased by 44 per cent, while in the central and northern regions of the Russian Soviet Federated Socialist Republic (RSFSR), which covers an area of 2,400,000 sq.km., it has decreased by 45 per cent and particularly between 1959 and 1967 this territory has lost 20 per cent of its rural population and nearly 40 per cent of its kolkhoz families. Furthermore, the areas which suffer most from emigration are usually thinly populated (Siberia) areas, while those where the rural population is increasing (like Moldavia and northern Caucasus) are already pretty densely populated.

The decrease in the population of kolkhoz is faster than that of the rural population because of the transformation of many kolkhozes into sovkhozes; a worker in the latter enjoys a higher and guaranteed wage and other advantages.

The new constitution defines the kolkhoz as a cooperative type of organization comprising peasants voluntarily united to work together on a socialist farm of large size based on pooled means of production and on collective labour. The distinction between indivisible kolkhoz funds' and the social share of each member of the *artel* has been abolished. Several writers have recently deplored the deviation of kolkhozes from the federative type towards independent farming controlled by the State. The constitution specifies three categories of interests viz. of the State, of the kolkhoz itself and finally the rights and duties of the its members. Kolkhoz must use the land—which belongs to the State—suitably, improve its productivity, by way of irrigation, drainage, soil conservation, etc. It requires to keep a balance between consumption and investment and insists that a part of its income must be put to investment.

The output is based upon production plan approved from time to time by the general assembly of the kolkhoz members, which must bear in mind the Government's purchasing plan. The output and work organization—through sectors, livestock farms, brigades, squads (*zvenos*) etc.—shall be organized in each kolkhoz according to the particular conditions of its economy. In very large kolkhozes, the production sector is subdivided into brigades. An important feature of the new constitution is the disappearance of the *trudodni*, meaning conventional days of work arranged on a sliding scale according to which various jobs were classified. At present guaranteed minimum rates are fixed in advance and a dividend distributed each month and then at the end of the year they are supplemented by extra dividends.

Alongside the organization of output and the regulation of work in agriculture, the model constitution has taken into consideration another important feature of life in the kolkhoz i.e. light subsidiary industries. Kolkhozes may also join together into kolkhoz unions or with State enterprises for specific purposes. At present there are 4000 such associations, of which over 2000 are engaged in building, 781 in poultry or cattle fattening etc. They may also engage in social activities such as hospitals, old peoples' homes, etc.

[*Monthly Bull. of Agric. Econ. and Stats, FAO*, **19** (9) (1970), 1]

FAO Study Group on Rice

The fourteenth session of the Study Group on Rice held in Rome during May 25-29 reviewed the world rice situation and outlook, identified the main problems facing the rice trade and decided to set up an inter-governmental *ad hoc* working party to recommend concrete measures to stabilize the world rice trade. The review showed that the world trade in rice declined in 1969 for the fourth successive year. Unlike 1966 and 1967, the lower import demand was the main factor behind the fall in world trade in the past two years. Reflecting the easier supply conditions,

export prices fell and carry-over stocks increased. The value of world rice trade declined by 10 per cent and export earnings in rice for most exporting countries dropped further.

The same broad trends seem likely to continue for 1970. Paddy production has risen in the current season and at 193 million tons (excluding mainland China, N. Korea and N. Vietnam), exceeds the previous season's record crop by 4 per cent. Export availablities in 1970 have been substantially augmented, whereas import requirements appear to be lower or about the same.

Hence, international prices are likely to average lower. Competition among exporters is likely to be further intensified and there will probably be some additional carry-over stocks. The governments of several exporting countries are curtailing rice production in 1970-71 season and others are reconsidering their production policies in order to avoid the prospects of mounting carry-overs of unsold rice.

The study group also undertook a comprehensive analysis of rice situation and likely future trends and patterns with a view to identifying all major economic problems affecting trade. The introduction of the new high-yielding varieties and national rice policies were the two main factors contributing to recent developments in the world rice economy.

The high-yielding varieties have so far made significant progress only in a few countries. There were several technical, economic and institutional problems still to overcome, and there were ecological limitations on their introduction in some areas. Nontheless, the new varieties had demonstrated a clear economic advantage over the traditional varieties in many areas. Recent studies carried out in the International Rice Research Institute, Philippines have shown that the introduction of the new varieties was likely to shift the comparatively in-producing rice for export. Therefore, the progressive adoption of high-yielding varieties in more countries over wider areas which are taking place will have important economic and trade implications and is likely to cause significant changes in trade patterns. The result of acceleration in production will also make it more difficult to plant so that supply and demand remain in equilibrium at reasonably remunerative prices.

As regards the second principal factor affecting the world rice situation, the group agreed that stability in international trade is closely linked with national production and price policies. To secure a balance between supply and demand in the international market, it is necessary to avoid conflicts between the basic aims of national policies. These inconsistencies cause instability in world trade with serious repercussions on the economics of countries heavily relying on exports. The study group identified the following major trade problem areas confronting world rice trade at present (i) a fall in commercial import markets, possibly accompanied by an expansion of exportable supplies, (ii) instability in prices, possibly with a declining trend in prices, (iii) accumulation of surplus stocks in some developed countries and possibly in certain developing countries as well, (iv) the increased role of rice for export on subsidized and concessional terms by developed countries and imposition of non tariff barriers to imports, (v) a dimishing share in world of developing exporting countries heavily dependent on rice exports (vi) the persistent gap between effective import demand and the physical and nutritional requirements of some developing importing countries, owing to balance-of-payments difficulties and the inability for ecological reasons, to take advantage of high-yielding varieties.

[*Monthly Bull Agric. Econ. and Stat*, *FAO*, **19** (6) (1970), 10]

Solvent Extraction Process for Nitrophosphate

The first commercial nitrophosphate plant using solvent extraction process is coming up at Oulu, in northern Finland. The plant is being set-up by Typpi Oy (Oulu), a Finnish company, which is engineering the solvent-extraction portion of the plant; Friedrich Uhde GmbH (W. Germany) is handling the engineering for the rest of the facility. The process has got many advantages, e.g. phosphate rock containing impurities can be used as feed material. Product is high-grade, with very high nutrient content and excellent phosphorus water-solubility. Additionally, solvent losses are minimal, and process requirements are modest.

In the Typpi Oy process, phosphate rock is dissolved in nitric acid. (Apatite from the Kola peninsula, and 56-60 per cent acid have been used in the pilot plant.) After crude insolubles have been separated out, the phosphate solution is fed into a ten-stage mixer-settler-extractor. The extraction of phosphate solution is technically difficult to achieve because of the insolubles and natural surfactants present. If the feed of the nitric acid to the extractor is not correct, monocalcium phosphate will precipitate, blocking the unit and decreasing the yield. Moreover, many solvents, such as n-butanol and isobutanol, react violently with nitric acid if they are mixed at certain ratios or at too high temperature.

Typpi Oy solved the problems by designing a new type of extractor, and by using tertiary amyl alcohol as the solvent (it is safe under even extreme conditions). In the extractor, phosphoric acid and fraction of the nitric acid transfer into the organic phase. The loaded solvent stream is then treated with a 50 per cent ammonium nitrate solution to remove calcium and other impurities. The result is very pure mixture of the acids in the organic phase. Calcium and other impurities are left in the aqueous phase. The organic phase is then neutralized with ammonia and sent to gravity settler. There, it is separated into a clear solvent layer and an aqueous nitrophosphate slurry containing ammonium phosphate and ammonium nitrate crystals. Over 99 per cent of the tertiary amyl alcohol is removed from the settler and, recycled. The remaining solvent is recovered by sending the aqueous slurry through an azeotropic distillation operation. Overall solvent losses are very low. The end product is 26:26:0 and by adding potassium salt, 18:18:18 product can be obtained. Water solubility of the product is 99% and P_2O_5 yield is 98.5%.

The solvent-extraction method is covered by patents in a number of countries (e.g. UK. 1,129,793 and 1,125,720) and has patents pending in several other nations.

Typical Needs per Ton of 18-18-18 product and 0.6 ton of 80% Ammonium—Nitrate Solution*

Item	Quantity
Investment	\$ 4 million
Raw materials	
Apatite	0.467 ton
Nitric acid (100 %)	0.814 ton
Ammonia	0.262 ton
Potash (60% K_2O)	0.300 ton
Carbon dioxide	0.165 ton

Contd. on p. 88

* Based on a plant with capacity of 550 tons of 18-18-18 product per day and 330 tons of 80% ammonium-sulphate solution per day.

Utilities

Steam (7.5 atm. abs.)	0.225 ton
Steam (2.5 atm. abs.)	0.217 ton
Electricity	45 kWh
Fuel Oil	60 lb.
Cooling water	7,700 gal.
Process water	48 gal.
Solvent	<4 lb.

[*Chem. Engng.*, Jan. 11, 1971, 63]

Recent Advances in Fertilizer Technology

The Fertilizer Association of India (FAI) will hold a 3 day seminar jointly with International Superphosphate and Compound Manufacturers' Association Ltd. (ISMA) in New Delhi during December 6-8, 1971 on Recent Advances in Fertilizer Technology. The following is the tentative list of papers offered for presentation at the seminar: (1) Ammoniation Reactions of Wet-process Phosphoric acid, Prof. J. Ando and T. Akiyama, Chuo University, Japan: (2) Developments in the Design, Engineering and Fabrication of Phosphoric Acid Plants in India, K. V. Mathew, FACT, Alwaye, India; (3) Indian Phosphate Rock in Fertilizer Industry, D. C. Gami, V. A. Sanghani and S. L. Agarwal, Gujarat State Fertilizer Co. Ltd., Baroda, India; (4) Problems of Transport, Storage and Handling of imported phosphoric acid, P. N. Arunachalam and K. Ranganathan, Madras Fertilizers Ltd., Madras, India; (5) Phospho-gypsum Beneficiation process, Taro Yamaguchi, Onoda Chemical Industries Co. Ltd., Japan; (6) Urea-based Compound Fertilizers, Mitsui Toatsu Chemical, Japan; (7) The Use of Urea as Nitrogen Source in Granular NPK Fertilizers, e.g. 19: 19: 19, Fisons Ltd., U.K.; (8) The Use of Urea and Superphosphate in the Production of Granular Fertilizers, Tennessee Valley Authority, USA; (9) Process for Obtaining New Reaction Products of Phosphoric Acid, Urea and Ammonia and Their Application in the Fertilizer Industry, M. Gittenait, Ugine-Kuhlmann, France; (10) Experiences in Construction and Operation of a Urea-Ammonium Phosphate (28-28-0) Plant, S. Prasad, Coromandel Fertilizers Ltd., Vishakapatnam, India; (11) The Continuous Use of Diluted Sulphuric Acid (scrubber acid) in the Production of High Analysis NPK Fertilizers, A. W. Heino, Eino Uusitalo and Erkki Aalto, Rikkihapo Oy, Finland. (12) Production of liquid and prilled NP and NPK fertilizers based on ammonium polyphosphate, M. Katlarevsky, Etab. Gardiner, France; (13) Manufacture of IBDU and Compound fertilizers containing IBDU, Noriyoshi Yanai, Mitsubishi Chemical Industries Ltd., Japan; (14) Suni Nitro, Mituo Tokunaga, Fuji Fertilizer Plant on Asahi Chemical Industry Co.Ltd., Japan; (15) New experiences with the Kampka-Nitro Process, K. Tesche, Chemische Fabrik Kalk, Germany; (16) Complex Fertilizer Technology and its Application, S. K. Mukherjee and P. K. Bhattacharjee, FCI Ltd. New Delhi; (17) Development of Phosphate rock and Pyrites Resources in India, M. L. Sethi, Director of Mines & Geology, Government of Rajasthan, Udaipur, India; (18) Treatment of Effluents from Phosphatic Plants, Prof. S. J. Arceivala, B. B. Bhale Rao, S. R. Alagarsamy and S. Rajagopalan, Central Public Health Engineering Research Institute, Nagpur, India; and (19) Packaging of Fertilizers, N.V.R. Iyengar and G. S. Bhome, Indian Institute of Packaging, Bombay, India.

ERRATUM

TECHNOLOGY Vol. 7 (1970), No. 4, Oct.-December 1970
On page 319 2nd Column 4th para under Results & Discussion E may be read as $E\frac{1}{2}$

News in Brief

Chemico's Thermo-Urea Process

The process recycles carbamate decomposition products in gaseous form by the use of multi-stage centrifugal compressor. Since the technique does in fact use a centrifugal compressor, it is only applicable in large plants with high gas throughputs, but in such a plant with a capacity of 600 tpd or greater it is claimed that striking economy can be realized. Carbon dioxide, ammonia and water vapour, produced at various pressures in the step-by-step decomposition section, are passed directly to corresponding pressure stages of the multistage compressor and recompressed in gaseous form to the synthesis reaction pressure. In this way, carbamate decomposition products are manufactured in stages at the least pressure drop required for their generation, so that considerable quantities of carbon dioxide and ammonia are produced at relatively high pressure. Although high pressure conditions are favourable to the formation of carbamate from carbon dioxide and ammonia, the compression step provides heat to the gases, thus retarding carbamate formation, so that corrosion problems, which could be very serious indeed for a centrifugal compressor, are eliminated completely. Reaction temperature is maintained by cooling a portion of the reactor effluent, and simultaneously producing low pressure steam.

Equipment such as carbamate pumps and carbamate condensers are no longer required. The need for process cooling water is eliminated and steam requirements are reduced, since low pressure steam is produced in the process by the high temperature condensation of reactor effluent. The use of a centrifugal compressor obviously entails the increased consumption of high pressure steam and/or electric power, but it is claimed that these are more than balanced by the output of steam in the process.

There have as yet been no customers for this process but it seems probable that if world urea demand continues to grow so that large capacity installat.ons are feasible, the Thermo-Urea process will have a significant impact on the urea industry in the future.

[*Nitrogen*, No. 64 (1970), 23]

PATENTS*

Ammoniating Solution for Making Slow-Release Nitrogen Mixed Fertilizers, by R. J. Church (to E. I. DuPont de Nemours & Co.)

U.S. 3,15,533, June 2, 1970, Appl. May 17, 1967; 4pp. The Urea-HCHO ammoniating solutions described in U.S. 3,438,764, (FA 2,966) can be improved by adding 1-30% NH_4NO_3 to decrease the salting-out temperature and improve stability in storage of the solutions. The range of composition is NH_3 10-20, urea 20-40, HCHO 20-50, water 10-20, NH_4NO_3 1-130, and CO_2 0-7 wt %.

[*Fertilizer Abstracts*, **3** (9) (1970, 211]

Urea Synthesis, by Eiji Otsuka, et al (to Mitsui Toatsu Chemicals, Inc.)

U.S. 3,514,483, May 26, 1970, Appl. Japan Nov. 26, 1965; 8 pp. The effluent from a urea synthesis reactor is cooled, the pressure is reduced to atmospheric, and it is mixed with an adduct-forming hydrocarbon such as n-hexadecane. The resulting urea-hydrocarbon adduct is crystallized from the solution and decomposed to urea and the hydrocarbon. The solution from the adduct separation can be used for producing fertilizers or it can be recycled (after concentration) to the urea synthesis reactor. For example, a urea synthesis reactor effluent, containing urea 60, NH_3 34 CO_2 44, and H_2O 18 parts, was cooled to 70°. The solution was fed, together with 27 parts water, to a vessel maintained at 32° where 10 parts n-hexadecane was added. The resulting adduct crystals were separated in a centrifuge; the 47 parts adduct was heated to 1.30° in a tank, forming a bottom layer of molten urea (38 parts) and a top layer of 9 parts n-hexadecane. The urea melt was dried and prilled, yielding 32 parts granular urea containing 0.5% biuret. The solution from the centrifuge, containing urea 28, NH_3 32, CO_2 42, H_2O 43, and n-hexadecane 1 part, was treated to remove the n-hexadecane and used to produce fertilizer.

[*ibid*, 211]

Urea Synthesis, by T. O. Wentworth (to Allied Chemical Corp.)

U.S. 3,514,484, May 26, 1970, Appl. Aug. 29, 1968; 3 pp. A two-step method for decomposing liquid $NH_4NH_2CO_2$ in urea synthesis effluent is described. The decomposition takes place in two heated zones; in the first liquid and formed vapors pass concurrently while in the second a thin film of liquid containing undecomposed $NH_4NH_2CO_2$ is passed by gravity over a heated surface and the vapors formed pass countercurrently. All vapors formed in the two zones are removed in a single zone maintained at a common pressure with that of both decomposition zones, located downstream form the first zone and vertically above the second. The decomposition vessel is described.

[*ibid*, 211]

Recovering Phosphorus from Sludge, by J. A. Hinkebein (to Monsanto Co.), U.S. 3,515,515, June 2, 1970, Appl. July 22, 1968; 7pp.

Division of U.S. 3,436, 184, (FA 2, 790). The P content of sludge produced in condensing P vapor is decreased by the presence of an oxidizing agent such as CrO_3 in the condenser liquor.

[*ibid*, 212.]

Granular Diammonium Phosphate, by R. S. Wiener (to Chemical Construction Corp.). U.S. 3,514,255, May 26, 1970, Appl. Apr. 30, 1969; 5pp.

Phosphoric acid is sprayed into a moving bed of recycled product fines in a device

* These patents have been reproduced from Fertilizer Abstracts, published by the National Fertilizer Development Centre, TVA, Muscles Shoals, Alabama USA, with kind permission of the Editor FA—**Editor**

such as a pan granulator. The resulting wet or damp solids flow to a rotary drum ammoniator equipped with an NH_4 sparger. The heat of ammoniation drives off appreciable water, and the granules discharged from the ammoniator contain not over 1% moisture. The granules are screened and the fines are recycled to the pan. The gases from the ammoniator are scrubbed with the incoming H_3PO_4 to recover NH_3. The method permits the use of concentrated H_3PO_4 (30% P_2O_5) and produces substantially dry granules from the ammoniator.

[*ibid*, 213]

Ammonia Synthesis Gas from Liquid Hydrocarbons, by W. L. Slater (to Texaco, Inc.) U.S. 3,520,823, July 21, 1970, Appl. Apr. 24, 1967; 7 pp.

A liquid hydrocarbon such as usually used as feed stock for synthesis gas generation (naphtha, whole crude, gas oil, etc.) is contacted at 400-650°F. and 1500-2650 psig with sea water or brackish water. The operation results in the formation of two liquid phases; an aqueous phase containing nearly all of the salts, and an organic phase comprise of a complexed solution of water in the hydrocarbon, substantially free of inorganic compounds. The organic phase can be fed directly into a synthesis gas generator instead of the usual separate feeds of hydrocarbon and water. The process is especially useful in regions where gaseous hydrocarbons and/or fresh water are not available for NH_3 manufacture. The hydrocarbon-water solution permits better control of the synthesis gas generator and the use of less water compared with the usual separate feeds.

[*ibid*, 3 (10) (1970), 237]

Beneficiation of Phosphate Rock Containing Limestone, by W. A. Blann (to Allis-Chalmers Manufacturing Co.) U.S. 3,522,012, July 28, 1970, Appl. Mar. 17, 1967; 9 pp.

Phosphate ores containing limestone as impurity are treated to form calcined flakes according to the method of U.S. 3,396,952 (FA 2, 163). The flakes are cooled and fed to an inclined, air-swept, rotating drum in which they are contacted with steam. The CaO is hydrated to $Ca(OH)_2$ accompanied by decrepitation which liberates the $Ca(OH)_2$ from the phosphate particles. Air classification serves to separate the $Ca(OH)_2$ particles from the phosphate particles.

[*ibid*, 238]

Enrichment of Phosphate Rock, by J. G. Kronseder and D. W. Leyshon U.S. 3,518,072, June 30, 1970, Appl. Nov. 3, 1966; 4 pp.

In beneficiating phosphate rock by calcination, the hot product from the calciner, at 600-1200°F., is sprayed with dilute H_3PO_4 whereby the material is cooled and enriched with P_2O_5.

[*ibid*, 238]

Pelletizing Phosphate Rock for Electric Furnace Feed, by Knapsack A. C. Brit. 1,198,223, July 8, 1970, Ger. Appl. May 12, 1967; 3 pp.

Sprayable suspensions containing 8-30% clay and 15-30% precipitator dust (by-product from electric furnace production of elemental P) are made by preparing a clay suspension containing 0.2-1.0% (clay basis) of a condensed alkali metal phosphate. The precipitator dust is added to the clay suspension. The suspension is used as a binder in pelletizing phosphate rock for use in electric furnace P production. (Cf. Fr. 1,406,141, CA 65, 1828c).

[*ibid*, 238]

Sueprphosphates, by A. E. Henderson U.S. 3,519,387, July 7, 1970, Appl. Dec. 7, 1967; 4 pp.

In reacting phosphate rock with H_2SO_4 or H_3PO_4 to produce superphosphates, the rock is preheated to 500-900°F. and the acid to 250°F. The use of preheated rock and acid, and vigorous mixing, promotes liberation of F and eliminates extensive curing. For example, 200 g phosphate rock (containing 34% P_2O_5, 49% CaO, and 4% F) was heated to 650°F. and mixed in a high-speed mixer for 15 seconds with 280 g 86% H_3PO_4 (containing 6 g diatomaceous earth) preheated to 300°F. The reaction mixture was cured for 45 minutes at 400°F. and cooled to room temperature. The product contained total P_2O_5 57.0, water-soluble P_2O_5 50.7, F 0.8, and H_2O 1.4%.

[*ibid*, 239]

Fertilizers Containing Potassium Metaphosphate, by Fisons Fertilizers Ltd. (by D. C. Harper and B. M. J. Ellul) Brit. 1,95,035, June 17, 1970, Appl. Sept. 20, 1967; 4 pp.

By mixing urea with $(KPO_3)_n$ were $n=$ 10-200 the $(KPO_3)_n$ is not complexed appreciably by the soil and the phosphate is quickly dispersed and is able to buffer the NH_3 released by the urea and 25 parts $(KPO_3)_n$ was heated to 135° and stirred, forming a dispersion of $(KPO_3)_n$ in molten urea. The mixture was prilled in a cooling tower. The granular product was 34.8-13.8-9.1 grade and completely soluble in water. Brit 1, 195, 332. Ammonium phosphate nitrate is used instead of urea. For example, 1.9 parts $(KPO_3)_n$ was stirred into 155° melt of 7.5 parts ammonium phosphate nitrate (containing 28.5% N and 11.8% P_2O_5). The mixture was prilled into KCl dust giving a 21.3-19.4-10.7 grade product.

[*ibid*, 239]

Ammonium Polyphosphate Produced at Atmospheric Pressure, by T. D. Farr and H. K. Walters (to Tennessee Valley Authority) U.S. 3,520,652, July 14, 1970, Appl. Oct. 2, 1968; 6 pp. Division of U.S. 3,484,192 (FA 3,192).

In the ammoniation of polyphosphoric acid containing over 80% P_2O_5 with concurrent hydrolysis of objectionable long-chain phosphate species, an intermediate slurry (pH 7.4-8.9) is prepared at 70-110° and processed further to produce solid ammonium polyphosphate fertilizers. (Cf. f.FA 3, 1067).

[*ibid*, 240]

Nitrophosphate Process, by J. F. Villiers-Fisher and A. J. Andreatch (to Chemical Construction Corp.) U.S. 3,518,071, June 30, 1970, Appl. Jan. 23, 1967; 5 pp.

Phosphate rock is digested with 60% HNO_3 using a HNO_3; CaO mole ratio of 2.5:1. The extract slurry is clarified by adding a flocculating agent and thickening. The clarified solution is mixed with a solution from a later step and the mixture is extracted with a water-immiscible organic solvent such as isoamyl alcohol. The organic phase from the extraction contains H_3PO_4, HNO_3, and a minor amount of $Ca(NO_3)_2$. The aqueous phase is primarily $Ca(NO_3)_2$ solution. The organic phase is then extracted with an aqueous solution (containing HNO_3, H_3PO_4, NH_4NO_3, and ammonium phosphate) from later step, whereby nearly all the $Ca(NO_3)_2$ and small amounts of HNO_3 and H_3PO_4 are dissolved into the aqueous phase. The resulting organic phase is then extracted with a concentrated aqueous solution (of NH_4NO_3 and ammonium phosphate) from a later step whereby the HNO_3 and H_3PO_4 enter the aqueous phase. The depleted organic phase is recycled to the first extraction step. The aqueous solution is ammoniated forming a solution containing NH_4NO_3 and ammonium phosphate. This solution is evaporated to form a slurry of NH_4NO_3

and ammonium phosphate crystals. The mixed crystals are separated from the mother liquor and dried to produce solid product. All or part of the mother liquor is recycled to the second extraction of the organic phase. The $Ca(NO_3)_2$ solutions from the foregoing operations are combined and treated with NH_3 and CO_2 to produce NH_4NO_3 by usual methods. The principal novelty of this process is the use of mother liquor from the NH_4NO_3—ammonium phosphate crystallization step to extract H_3PO_4 and HNO_3 from the organic solvent. This feature avoids the dilution with large amounts of water that usually accompanies this step. The products are substantially free of $Ca(NO_3)_2$.

[*ibid*, 240]

Nitrophosphate Process, by Samuel Strelzoff, Abe Warshaw, J. F. Villiers-Fisher, and Syndney Atkin (to Chemical Construction Corp.) U.S. 3,518,073, June 30, 1970, Appl. Jan. 23, 1967; 10 pp.

Phosphate rock is digested with HNO_3 and the resulting solution is extracted with a water-immiscible organic solvent, such as amyl alcohol, to remove H_3PO_4 into the organic phase while leaving $Ca(NO_3)_2$ in the aqueous phase. The organic phase is then extracted with water to produce H_3PO_4 which can be ammoniated to produce ammonium phosphate. When sufficient HNO_3 is used in the digestion to permit selective extraction of the phosphate values, HNO_3 will be recovered along with the H_3PO_4 and in this case ammoniation of the product acid will produce NH_4NO_3 and ammonium phosphate. (Cf. FA 3, 1588).

[*ibid*, 240]

Granulated Fertilizers, by B. G. Smith U.S. 3,516,813, June 23, 1970 Appl. July 1, 1968; 5 pp.

In producing granulated fertilizers by adding liquid and solid raw materials to recycled solids the particle size of the feed solids is regulated so that over 50% is only slightly smaller than the minimum product size. A more uniformly-sized product is thereby produced.

[*ibid*, 241]

Fertilizers Containing Micro-and Macronutrients, by O. D. Philius Silverberg, and M. M. Norton (to Tennessee Valley Authority) U.S. 3,520,651, July 14, 1970, Appl. June 28, 1968; 7 pp. Division of U.S. 3,423,199 (FA 2,333).

The compound $3Zn(OH)_2 . NH_4NO_3$ is claimed as a new composition of matter. The compound can be formed in situ on the surface of granular fertilizers by the methods described in the earlier patent.

[*ibid*, 241]

Fertilizers Containing Micro and Macronutrients, by O. D. Philen, Julius Silverberg, and M. M. Norton (to Tennessee Valley Authority) U.S. 3,523,019, Aug. 4, 1970, Appl. Sept. 4, 1969; 7 pp. Division of U.S. 3,520,651 (FA 3,1594).

Granules of hygroscopic fertilizer salts are coated with micronutrient powders which, when wetted with water and/or steam, react to form *in situ* stable compounds such as $Zn_3(NH_4)_2(P_2O_7)_2.2H_2O$ or complex zinc ammonium hydroxy nitrates. The complex fertilizer compounds maintain good physical properties of the fertlizers in addition to providing available micronutrient.

[*ibid*, 241]

Suspension Fertilizers, by H. Trimbach and A. Villiard (to Potasse et Engrais Chimiques) U.S. 3,519,413, July 7, 1970, Fr. Appl. July 24, 1964; 3 pp.

In preparing fertilizers comprised of aqueous/fluid suspensions of fine crystalline fertilizers (for example, by ammoniation of a mixture of HNO_3 and H_3PO_4) addition of 0.3.4% of a gum such as guar or locust bean flour stabilizes the suspension against settling, without materially increasing the viscosity.

[*ibid*, 242]

Nitrogen Fixation by Ionizing Radiation, by R. I. Miller (to Aerojet-General Corp.) U.S. 3,505, 189, Apr. 7, 1970, Appl. Nov. 25, 1960; 4 pp.

A solid polymeric composition containing N, C, and O is prepared by irradiation of a gas mixture of N and CO. In an example, several stainless steel 30cc capsules were loaded with a mixture of 90% N and 10% CO. at 1500 psia. Fissionable material was provided in the form of an open mass of fine glass wool containing U_3O_8 incorporated in a SiO matrix; there was 1.85 g 235 U/capsule. The capsules were N-cooled to 100°F. and irradiated for six hr. in the Livermore, California, pool-type reactor providing ionizing radiation having an energy disposition in the gas mixture in excess of 10^{20} eV/g gas. On removal from the reactor the capsules contained a light yellow powder containing N 13.3 — 0.8, 0 41.3± 14.7 and C 30.9± 15.8%. On heating in an open tube the solid started to darken at 80-100°. Some melting occurred at 130° and evaporation or decomposition was appreciable. At 170° the dark residue appeared to soften but did not melt completely 200°. Gases evolved during pyrolysis included CO_2, HCN, and $(CN)_2$. The product was soluble in water, formamide, formic acid, DMSO, and concentrated H_2SO_4. On hydrolysis the solid formed a strong acid (pK 4); for a 5g/1 concentration the pH was 2.4. The acid was not identified. On Kjeldahl analysis without a digestion step 26% of the N was obtained. Spot tests for NH_3 in the aqueous solution were positive. Such products should be useful as fertilizer components.

[*ibid*, 3 (11) (1970), 263]

Steam-Reforming of Light Hydrocarbons, by S. A. Guerrieri (to Lummus Co.) U.S. 3,524,819, Aug. 18, 1970, Appl. Mar. 3, 1967; 6 pp.

In the production of H by catalytic steam reforming of gaseous hydrocarbons a mixture of steam and hydrocarbon is fed into a bed of catalyst at a velocity sufficient to maintain the catalyst in fluidized state. The reformer temperature is maintained at 1400-2300°F. by withdrawing the catalyst and circulating it through a fluidized bed heater. In comparison with the usual fixed -bed catalyst in a plurality of externally heated tubes, the method permits the use of higher temperatures and pressures and is free of the mechanical and thermal problems associated with packed tubes.

[*ibid*, 263]

Inhibiting Loss of N From Urea, by P. R. Geissler, et al (to Esso Res. & Engineering Co.) U.S. 3,523,018, Aug. 5, 1970, Appl. Jan. 8, 1969; 3 pp.

Addition of urea inhibitors to a urea melt before prilling decreases loss of NH_3 from the urea when distributed on the soil surface. Addition of urease inhibitors as a surface coating on urea prills is ineffective. Borax or $CuSO_4$ are effective inhibitors when added to the urea melt in amounts from 0.1-10%.

[*ibid*, 264]

Briquetting Phosphate Rock for Electric Furnace Charge, by T. E. Kass and R. J. Gleason (to FMC Corp.) U.S. 3,522,338, July 28,1970, Appl. May 31,1968; 4 pp.

A mixture of washed phosphate rock and floation concentrate, of —35 +150 mesh

size, is prepared from Florida or North Carolina phosphate ore containing quartzite sand. The composition of the mixture is regulated to provide the proper SiO_2; CaO ratio (0.75—1:1) for electrothermal production of elemental P. The mixture is then heated to 1600—1900°F. in a fluidized bed or other type of calciner. The hot mixture is then compressed at high pressure between briquetting rollers. During the calcination, fine phosphate particles become attached to and surround the quartzite sand particles, forming agglomerates. In the briquetting rollers the phosphate becomes plastic and acts as a cement for the sand, producing a strong briquette. The phosphate also protects the briquette roll pockets from abrasion by the quartzite.

[*ibid*, 264]

Phosphoric Acid, by Yoshito Yasutake and Yosisige Fujita (to Central Glass Co., Ltd.) U.S. 3,523,754, Aug. 11, 1970, Japan Appl. Apr. 2, 1966; 4 pp.

In a process for the manufacture of H_3PO_4, phosphate rock is treated with H_3PO_4 and H_2SO_4 to form a slurry of gypsum. The slurry is mixed with seed crystals of $CaSO_4 \cdot \frac{1}{2}H_2O$ and the mixture is held at temperatures and SO_3 concentrations suitable for converting the gypsum to $CaSO_4 \cdot H_2O$. When the total concentration (P_2O_5 + SO_3) in the liquid phase is 40% the temperature is held above 75°. After conversion of the gypsum the slurry is filtered, yielding product acid containing at least 35% P_2O_5. The by-product $CaSO_4 \cdot \frac{1}{2}H_2O$ is of high purity. (See FA 1,978)

[*ibid*, 264]

Estimation of Sulfate Ion in Wet-Process Phosphoric Acid Slurry, by K. A. Sherwin (to Fisons Fertilizers Ltd.,). Brit. 1,173,152, Appl. July 1,1966.

The slurry is fed at constant rate into a mixing chamber, into which is pumped a liquid reagent, for example aqueous $BaCl_2$, that reacts with SO_4^{2-} to form a precipitate. The mixture is fed to a photo-electric detector for determining the turbidity, or other physical characteristic of the solution. Fluctuations in the turbidity are automatically controlled by varying the rate of supply of the reagent, which gives a measure of the SO_4^{2-} content of the slurry.

[*ibid*, 268]

Removing Magnesium from Phosphate Rock by Cominco Ltd., (by C. H. G. Bushell and H. E. Hirsch). Can. 839, 774, Apr. 21, 1970, Appl. July 8, 1966; 11 pp.

Most of the carbonates of Mg and Ca can be separated from phosphate rock by anionic froth flotation in the presence of a soluble inorganic fluoride. For example, phosphate rock (P_2O_5 30.3, CaO 45.5, MgO 0.9, SiO_2 10.6, and ignition loss 4.6%) was ground to —100 mesh and suspended in an aqueous solution containing 5g NH_4HF_2/1. The concentration was adjusted to 30-35% solids and the PH was brought to 5.8-6.0 by adding NH_4OH or HF. Flotation was conducted three times using a fatty acid as the flotation reagent. The concentrate (underflow) contained P_2O_5 31.4 CaO 45.8, MgO 0.3, SiO_2 11.0, and ignition loss 3.0%, The recovery of P_2O_5 was 92.6%; removal of Mg was 70%.

[*ibid*, 3 (8) (1970), 189]

Anhydrous Hydrogen Fluoride by R. J. Laran, et al (to Ethyl Corp.)- U.S. 3,501,268 Mar. 17. 1970, Appl. May 18, 1967; 4 pp.

Anhydrous HF is produced from byproduct H_2SiF_6 solution obtained in processing phosphate rock. Part of the H_2SiF_6 solution is treated with NH_3 and part with $Al(OH)_3$, filtering off the SiO_2 formed in each treatment. The resulting NH_4F filtrate is then reacted with the AlF_3 filtrate to precipitate $(NH_4)_3AlF_6$. The precipitate is filtered off and heated to 400—500° whereby it decomposes to a vapor containing NH_3 and NH_4HF_2 leaving a residue of AlF_3. The vapor is cooled to 130° causing crystallization of NH_4HF_2 which is separated from the NH_3 and treated with concentrated H_2SO_4 at 150—250°, forming anhydrous HF vapor and leaving a residue of $(NH_4)_2SO_4$.

[*ibid*, 190]

Phosphoric Acid Production by G. M. Lloyd and W. P. Banks (to Continental Oil Co.). U.S. d, 511, 604, May 12, 1970, Appl. Apr. 7, 1967; 2pp.

In calcining phosphate rock high in organic matter (for example North Carolina phosphate rock) the sulfide content is increased. When such material is used in the production of wet-process H_3PO_4 the corrosiveness of the acidulation slurry is increasd by the presence of the sulfides. For example a raw rock containing 40 ppm sulfide was calcined at 1300°F.; the calcined material contained 2660 ppm sulfide. The corrosion rate of Type 317 stainless steel by the raw rock + H_2SO_4 was 250 mills/yr whereas that by the calcined rock + H_2SO_4 was 697 mils /yr. Addition of As_2O_3 (0,021%, rock basis) to the acidulation vessel decreased the corrosion rate of the calcined rock slurry to 4 mils/yr.

[*ibid*, 190]

Ammonium Salts for Fertilizer Use by B. J. Kerley, Jr. U.S. 2,902,342, Sept. 1, 1959, Appl. Jan. 27, 155; 4 pp.

Ammonium phosphates and/or $(NH_4)_2SO_4$ are produced in solid form, substantially free of water, by stepwise ammoniation of H_3PO_4 and/or H_2SO_4. The acid is partially neutralized with anhydrous NH_3 to prepare a hot slurry having a residual acid concentration equivalent to 18-36% H_2SO_4. The hot slurry is then fed continuously under pressure to an elongated tubular reactor. Additional anhydrous NH_3 is also fed to the reactor in a proportion to yield a substantially neutral solid product. The reactor has a limited cross-section area to provide rapid flow of the reaction mixture. The mixture is discharged from the reactor with release of pressure into a cylindrical chamber with conical bottom where the water vapour is separated from the solid product. The reactor and separation chamber are described in detail.

[*ibid*, 191]

Recycling Ammonium Sulphate in Nitric Phosphate Processing, by O. W. Livingston (to Tennessee Valley Authority). U.S. 3,515,534, June 2, 1970, Appl. Sept. 30, 30, 1969; 11 pp.

Three improvements are described for the $(NH_4)_2SO_4$-recycle nitric phosphate process for producing N-P fertilizers from HNO_3 extracts of phosphate rock (Cf. FA 3,840). The filtrate from the gypsum removal step is ammoniated with gaseous NH_3 to pH 5.5-6.0 while being heated to boiling. This precipitates and agglomerates the impurities Ca, Fe, Al, and F. The resulting slurry is then further ammoniated to a pH of at least 9.3 while cooling to 60-85°F. The resulting slurry is readily filtrable. In the conversion of the gypsum to $CaCO_3$ and $(NH_4)_2SO_4$, use of minimum agitation results in the growth of agglomerates of $CaCO_3$ which have high filtrability. In the precipitation of the gypsum, a portion of the total requirement of $(NH_4)_2SO_4$ is added to the extractor during the treatment of the phosphate rock with HNO_3; the remainder of the $(NH_4)SO_4$ is added to the slurry from the acidulator in the usual way. This split application of

$(NH_4)SO_4$ results in improved filtrability of the gypsum.

[*ibid*, 191]

Chlorination of Rock Phosphate

Efforts are being made to replace sulphuric acid by other chemicals in the production of soluble phosphates from rock phosphates. Two alternative methods which are in experimental stage in India are (i) fusion of feldspar with rock phosphate and (ii) reaction of urea nitrate with rock phosphate.

In a new CSIR research scheme granted to Prof. V. Ramakrishna (principal investigator) of the Indian Institute of Technology, Delhi, it is proposed to work out conditions, for producing soluble phosphates from rock phosphate by chlorination. The conditions of chlorination, such as temperature, chlorine pressure, contact time, etc., will be studied to evolve a laboratory method, which will be scaled up for industrial application.

[*CSIR News*, **20** (21) (1970), 168]

Fertilizer Project in Goa

The Zuari Agro Chemicals Ltd. is setting up a fertilizer project in Goa in technical collaboration with US Steel Corpn. The company has been licensed to manufacture annually 220,000 tonnes of ammonia, 340,000 tonnes of urea and 0,000 tonnes of compound fertilizer. The main feedstock naphtha will be supplied by the Indian Oil Corporation from its proposed installation at Mormugoa and its annual requirement will be 200,000 tonnes. The capital outlay of the project is estimated at Rs. 56.55 crores with a foreign exchange component of Rs. 26.17 crores. The plant is expected to be ready by July 1972. The construction has been entrusted to Toyo Engineering Corpr. of Japan.

[*Oil Statistics*, (2) (1970), 21]

Potassium Chloride from Sea Bittern

There are no potash deposits in India and our requirements for potash fertilizer and chemical industries are mostly met by imports to the extent of 1.7 lakh tonnes of K_2O (1969). The only important source is bittern and from it about 40,000 tonnes of potassium chloride (15,200 te of K_2O) can be manufactured. The estimated reserve from the salt industry will be about 1.0 lakh tonnes in terms of K_2O.

The process know-how of recovery of potash from bittern developed by the Central Salt and Marine Chemicals Research Institute is covered by the Indian patent no. 67467. It consists of (i) recovery of mixed salt, containing 18-20 per cent potassium chloride, by solar evaporation of bittern; (ii) extraction of potassium chloride as carnallite in presence of magnesium sulphate from mixed salt; (iii) decomposition of carnallite to yield impure potassium chloride; (iv) recrystallization of impure potassium chloride; and (v) recovery of epsom salt and sodium sulphate as by products from the residue left in (ii).

Potassium chloride in 29°Be bittern is only 2-2.5 per cent; the evaporation of this bittern is carefully controlled and carried out in two steps—first to 34/34.5° to separate sodium chloride as crude salt with magnesium sulphate and then to 36.5°Be to obtain mixed salt containing 18-20 per cent potassium chloride, 15-20 per cent sodium chloride, 30-35 per cent magnesium sulphate, 6.8 per cent magnesium chloride, 1-2 per cent insolubles and rest water.

A plant for producing 1000 tonnes of potassium chloride, 2000 tonnes epsom salt and 900 tonnes of sodium sulphate requires Rs. 22.3 lakhs as capital investment (including for mixed salt production). The return on the investment is 36 per cent. Such a plant is in operation at United Salt Works, Kandla.

[*Salt Res. and Indus.*, **7** (2 & 3) (1970), 39]

The Apex Process for Manufacturing Phosphatic Fertilizers and Industrial Phosphates

A process to produce economically water-soluble P_2O_5 without the use of sulphur is made available by Azote et Produits Chimiques S.a. (France), using isobutyl alcohol as economic and flexible solvent for extracting the phosphoric acid and excess nitric acid. The two extracted acids are separated by neutralising the solution with ammonia.

The stages include the following: (i) *Digester*—nitric acid used for digesting the neutral phosphate rock (ii) *Extraction stage*—phosphoric acid extracted with isobutyl alcohol containing 3 per cent nitric acid. (iii) Purification stage—for removing the last traces of calcium from the alcoholic solution. (iv) Separator—for phase separation.

Other major variants of the process use hydrochloric acid or sulphuric acid for digestion. The aqueous solution leaving the extraction stage contains all the calcium and ammonium nitrate and after removal of the alcohol it is treated to ammonium carbonate to convert the calcium nitrate to ammonium nitrate. Under these conditions the overall yield of P_2O_5 is 98 per cent. The conventional version of the 'Apex' process yields monoammonium phosphate and ammonium nitrate from the nitric acid digestion liquor but there are many possible alternatives based on the common factors of the extraction of phosphoric acid and its regeneration by neutralization. Among the various possibilities for making monoammonium phosphate versatile, two recent developments appear to be worth mentioning: Conversion of N to NK by double decomposition and the purification of wet process phosphoric acid for producing alkaline phosphates directly for their final use in detergents. An economic evaluation shows that net cost of 1 ton of P_2O_5 after making allowance for ammonium nitrate amounts to about 480 francs for pure MAP and 450 francs for 19:38 binary (a mixture of MAP and A.N.).

[*Brit. Chem. Engng.*, **15** (9) (1970), 1113]

Fertilizer Factories During IV Plan

The fourth plan envisages minimum capacity and production targets of 3 million and 2.5 million tonnes of nitrogen for 1973-74. In regard to phosphatic fertilizer, a minimum capacity of 1.2 million and production of 0.9 million tonnes is envisaged for 1973-74. The estimated demand (consumption target) of nitrogenous and phosphate fertilizers is 3.2 and 1.4 million tonnes respectively for 1973-74; the target for potash is 0.9 million tonnes. The present status of the fertilizer programme, in the public and private sectors, is given below.

	Nitrogen, mil.te	P_2O_5 mil.te
Existing Capacity	1.344	0.421
Capacity Under Construction	1.210	0.431
Capacity Approved but yet to be firmed up	1.256	0.516
Capacity Approved in principle	1.158	0.555

(*Source*: Lok Sabha, Nov. 23, 1970)

[*Oil Commentary*, **8** (5) (1970), 21]

Additional Refining Capacity in Assam

A techno-economic feasibility study group recommended the expansion of Gauhati refinery from 0.75 to 1.75 mil.

tonnes/yr. After discussion with Assam ministers, a further study was made on comparative investment costs and returns of various alternatives. The Group, after making these comparative studies, reported that expansion of the refinery was still the more preferable alternative; but on overall considerations, partciularly advantages to be derived from the improvement of operations and profitability and increased production of Sindri fertilizer factory with the use of RFO (LSHS) as feedstock, a separate refinery could be agreed to. On this basis, a grass-root refinery of 1-million tonnes capacity at Bongaigaon could be supported provided LSHS from the refinery is taken to Sindri. The Assam Government has accepted the proposal but had gone on to add that secondary facilities be established at Bongaigaon for processing the surplus naphtha and LSHS. But it was thought prudent not to invest in the facilities. The State Government has since agreed to the central Government's proposal.

(*Source*: Lok Sabha: Nov. 30, 1970)

[*Ibid*, 18]

Mithapur and Goa Fertilizer Plants

Government have approved in principle the revised proposal of Tatas for the establishment of a fertilizer factory a Mithapur, subject to certain conditions. A letter of intent has accordingly been issued to Tata Chemicals Ltd. on July 25, 1970. Final decision in this matter will be taken on fulfilment of the conditions in the letter of intent by the party.

As regards Goa Fertilizer Project, an industrial licence was granted to Messrs Zuari Agro Chemicals Ltd. on 12.12.66. The financing proposal relating to this project was finally approved by the Government on 21.12.69.

According to the financing plan approved by the Government, the total equity capital of the company would be Rs. 1242.75 lakhs of which Rs. 437.25 lakhs will be held by Indians and Rs. 805.5 lakhs will be held by foreign parties including non-cash shares to the extent of Rs. 72.75 lakhs. The project is likely to be commissioned in the second half of 1972. The value of machinery and materials to be imported from USA, Japan and Europe is estimated at Rs. 14.53 crores. Several financial institutions of the Government have underwritten the shares of the company.

(*Source*: Lok Sabha: Nov. 30, 1970)

[*ibid*, 22]

Tuticorin Fertilizer Project

The letter of intent given to the Tamilnadu Industrial Development Corporation for the Tuticorin Fertilizer & Allied Projects has been transferred in favour of the Southern Petrochemicals Corpr. Ltd., No decision has yet been taken regarding the feedstock for the project.

[*ibid*, **8** (4) (1970), 12]

FACT Exports Fertilizers

Fertilizers & Chemicals Travancore Ltd. has despatched its first consignment of 28.5 tonnes of ammonium chloride bar to E. African countries against payment in pound sterling. The total order received from those countries is 166.5 M. tons valued at Rs. 2,27,000. The company has confirmed from UAR for 490 M. tonnes of ammonium chloride powder and 96 tonnes from a S-E Asiatic country. Negotiation for supplying ammonium chloride to Ceylon is in progress.

[*ibid*, **4** (8) (1970), 961]

Neyveli Lignite Corporation

There was overall increase in production at Neyveli during 1969-70. The gross profit was Rs. 1078 lakhs against Rs. 1073 lakhs in the previous year. The improvement ranged from 4 per cent in the briquetting and carbonization plant to 7.5 cent in the power plant; to 7.5 per cent in the mine and 8.3 per cent in the power plant; production in the urea plant (88,166 tonnes) shightly declined.

[*ibid*, 959]

New Corporation for Project Exports

Government of India have decided to set up a new corporation, a subsidiary of State Trading Corporation, to develop fully the country's export potential in the sophisticated fields. It will specialize in large ventures and turn-key products, particularly in the fields of (a) railway systems including locomotives and other rolling stock, track and signal equipments, etc., (b) public utilities, (c) complete industrial plants and projects, and (d) castings, forgings ancillary equipment for big international manufacturing concerns. It will develop special marketing and operational schemes to secure maximum possible exports from India in these fields. Its turnover has been estimated at Rs. 40 crores in 1970-71 and Rs. 60 crores in 1971-72.

The new organization will help the Indian industry in both public and private sectors in regard to the identification of marketing opportunities abroad, tendering and negotiations, finance and foreign exchange, quality control and delivery schedules.

[*Lok Udyog*, **4** (9) (1970), 1067]

Caprolactam Plant in Gujarat

The Gujarat State Fertilizer Co. is setting up a caprolactam plant at Rs. 26.7 crores with a foreign exchange component of Rs. 17 crores. When completed in the first half of 1973, the plant will have an ultimate capacity of producing 20,000 tons of caprolactam per year and will be ranked as one of the most modern in the world.

[*ibid*, 1077]

FCI Signs Contract with a Czech Firm

A supply contract under Indo-Czech agreement was signed on January 9 at New Delhi between Fertilizer Corporation of India and M/s Techno-Export Foreign Trade Co. Ltd. of Czechoslovakia for the supply of imported equipment and machinery for the air separation and nitrogen wash units of the two coal-based fertilizer plants being set up at Talcher (Orissa) and Ramagundam (AP).

New Rice Varieties

The International Rice Research Institute (IRRI), of Philippines has released 2 new rice varieties, IR 20 and IR-22. IR-20 has a medium grain, which is free of white belly and is slender, hard and translucent; its milling quality is high and cooking quality acceptable. It was developed from a cross of IR 262-24-3 and TKM 6 and compares with IR-8 in resistance to rice stem borer except that its yield is slightly less.

IR-22 has grain characteristics very similar to IR-20 except that it has a long grain. It was developed from a cross of IR-8 and Tadukan. It yields slightly more than IR-8 and matures a few days earlier than either IR-8 or IR-20. It is more resistant to lodging than IR-20 but less than IR-8. Both the new varieties are susceptible to brown plant hoppers and leaf hoppers.

[*FAI Inf. Serv.*, **12** (4) (1971), 3]

Asia-Pacific Food Conference

In inaugurating the 7th Asia-Pacific Food Conference held at New Delhi recently, Lala Bharat Ram, said that the very circumstances which made 'green revolution' possible had given rise to new and more

complicated factors. Apart from the imbalances and disparities in the pace of development, there was the realization that greater food production by itself was not enough. The rural population should be fed with more consumer foods and persuaded to invest their surpluses in productive channels. Earlier Mr. S. T. Keel, Vice-President, International Minerals and Chemical Corpr. and chairman of the Conference, said that the success of 'green revolution' had brought to light weaknesses in several critical areas—prices, credit, land reform, food storage and distribution to name a few.

Speaking at the first working session, Mr. S. M. H. Burney, Jt. Secretary, Union Ministry of Food & Agriculture, said that incentives offered to the farmers had enabled India to reach a 'take-off' stage. India has reached a stage from which it would be able to register dramatic advances in agriculture through the wise use of incentives, like sound price support, institutional support land reforms, link roads better local storage facilities and marketing opportunities.

Mr. Tonuma said that Japan produced 14.2 m. tons of rice against a demand 11.6 millions, so some rice land would be utilized for some other crops. There would be even 'retirement' of land in which case the farmers would be paid compensation at 30,000-45,000 yens (Rs. 620-930)/hectare crop area/annum.

The Malaysian delegate, Mr. Schwencke, stated that his Government had embarked upon a master plan to develop a palm oil industry in view of the competition natural rubber is facing in the international market due to the development of synthetic rubber. Each landless farmer is being given 10 acres of land as well as financial assistance to cultivate palm.

[*ibid*, **12** (3) (1971), 6]

Sulphur Removal from Gas

A new process designed for gas wells has been announced by Wintershall Ag., Kassel, W. Germany. The element sulphur present in the reservoir is carried by the gas from the bottom of the bore hole and separates out in the riser pipe to form a rock-hard deposit on the wall of the pipe. Accumulation of sulphur can shut down the well unless removed periodically by costly scraping, a time-consuming operation for which the well must be closed down temporarily.

Two gas fields in Germany have been equipped with the new process, which prevents the separation of sulphur in the riser pipe and provides for recovery of the sulphur at the well head.

A solvent injected into the bore hole carries the sulphur up the riser to the well head where a separator plant scrubs out the solvent and sulphur in a single stage. The solvent is returned to the bore hole, and the sulphur is recovered.

(*Source*: Financial Times: July 27, 1970)
[*Oil Statistics*, **8** (3) (1970), 28]

Vitamins from Petrochemicals

Badische Anilin and Soda Fabrik, Ludwigshafen, has developed a continuous process for manufacturing vitamins A and E from cheap petrochemical raw materials, the capacity of the expected plant being 1,000 tons/year. Though the process has not been disclosed in detail, the feedstock is believed to be formaldehyde and iso-isobutylene. An initial step is production of methylpentone. For vitamin production, this is converted into isophytol which combines with trimethylhydroquinone to yield the vitamin itself. In vitamin A manufacture, the methylpentone is processed into C_{15} compound and is combined with C_5 compound obtained from propargh-yaldehyde via a wetting reaction.

(*Source*: Popular Plastics: July, 1970)
[*Oil Statistics*, **8** (3) (1970), 29]

Activities in FCI

1971 marks the completion of a decade of existence of Fertilizer Corporation of India which came into existence on Jan. 1, 1961 with the amalgamation of Sindri Fertilizers & Chemicals Ltd, and the Hindusthan Fertilizers & Chemicals Ltd. It has now an authorized capital of Rs. 200 crores with an annual installed capacity to produce 4,10,325 tonnes of nitrogen and 36,000 tonnes of phosphate (P_2O_5). Its five operating units, viz. at Sindri, Nangal, Trombay, Gorakhpur and Namrup, during 1969-70 produced 3 lakhs tonnes of nitrogen and 17,000 tonnes of phosphate. Its 4 new major projects in the implementation stage are at Dargapur, Barauni, the Namrup expansion and the Sindri rationalization scheme.

Besides, the FCI has undertaken the responsibility of setting up 3 coal-based fertilizer plants, each costing about Rs. 75 crores and production capacity of 900 and 1500 tonnes of ammonia and urea daily (2,28,000 tonnes of nitrogen annually).

The Government of India have already approved in principle a Rs. 73 crores fertilizer project at Haldia (W. Bengal), based on fuel oil available in the country. It will have an annual capacity to produce 3,77,000 tonnes of introphosphate, 165,000 tes of urea and 60,000 tonnes of soda ash.

Fabrication of Crystallizer at Sindri: The fabrication wing of the Central workshop of Sindri fertilizer factory has successfully fabricated a stainless steel crystallizer plant for their ammonium sulphate plant. It measures 5,944 mm. in height and 4420 mm. in diam. at the maximum cross-section. It is of 316 S S material and contains twenty nozzles of varying dimension. Except the stainless steel, all other materials used in the fabrication were procured indigenously.

Fabrication of Condenser of Nitric Acid ?lant: The Nangal Units' mechanical worshop fabricated a shell and tube type condenser containing 1003 tubes at an expenditure of Rs. 1.5 lakhs against the market price of Rs. 2.6 lakhs. The complete condenser weighs about 11.5 tonnes, which includes about 5-6 tonnes of special stainless steel It's overall dimensions are: 1.42 metres diam. and 6.6 metres length.

[*Fertilizer Digest*, **9** (2) (1971), 18]

A New Division in FCI

Fertilizer Corpr. of India Ltd. is going to establish shortly an industrial products division to market the industrial products of all its units and divisions and to indicate action on new product development and exports. This division would also be concerned with exports of industrial products. Besides several fertilizers, FCI is already marketing a number of industrial products, such as sulphuric acid, nitric acid, ammonium bicarbonate, technical grade urea, methanol, argon gas anhydrous ammonia from its Trombay unit and nitric acid, anhydrous ammonia, ammonium bicarbonate and industrial solvents from Sindri Unit. The total value of these products is about Rs. 6 crores. The area of operation covered is Maharashtra, W. Bengal, Delhi Madras, Andhra Pradesh and Mysore.

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Bharat Heavy Electricals Ltd., a public sector organization, have recently signed an agreement with Nuvo Pignone of Italy to undertake manufacture of centrifugal compressors required for the fertilizer and

chemical industries at their plant at Hyderabad.

[*FAI Inf. Serv.*, **12** (4) (1971), 11]

The Minerals and Metals Trading Corpr. (MMTC) will import 3 lakhs tons phosphate valued at Rs. 2.5 crores from Jordan during 1971. The entire purchase of rock phosphate will be balanced through exports of tea and non-traditional goods to Jordan.

[*ibid*, 6]

India is well poised for a revolution in a number of agricultural products, like rice and cotton production, according to Dr. M. S. Swaminathan, Director, Indian Agricultural Research Institute. He told the concluding session of Asia-Pacific Food Production Conference, held recently at New Delhi, that India now possessed the scientific tools and competence to achieve a major technical change in agriculture.

[*Ibid*, **12** (3) (1971), 8]

STATISTICS

TABLE 1—Public & Private Fertilizer Projects during IV Plan

	Capacity in '000 tonnes in terms of Nitrogen (N) and Phosphates (P_2O_5)		Location	Name of the Concern
1	2		3	4
	I. Projects finally approved during the Fourth Plan			
A. Public Sector	N	P_2O_5		
(1)	229	—	Talcher (Orissa)	Fertilizer Corpn. of India Ltd.
(2)	229	—	Ramagundam (Andhra Pradesh)	-do-
(3)	132	132	Trombay (Maharashtra)	-do-
B. Co-operative Sector				
(4)	215	127	Kalol & Kandla (Gujarat)	Indian Farmers Fertilizer Co-operative Ltd.
C. Private Sector				
(5)	175	45	Goa	M/s. Zuari Agro-Chemicals Ltd. (Their financing plan was finally approved on 31.1.69)
	II. Projects under consideration which if finally approved may be commissioned in Fourth Plan			
A. Public Sector				
(1)	54	137	Cochin (Expansion) (Kerala)	Fertilizer & Chemicals Travancore Ltd.
(2)	152	70	Haldia (West Bengal)	Fertilizer Corpn. of India Ltd.
B. Private Sector				
(3)	160	—	Mangalore (Mysore)	Malabar Chemicals & Fertilizers Ltd.
(4)	248	69	Tuticorin (Tamil Nadu)	Southern Petro-chemicals Industries Corporation Ltd.
(5)	22	—	Kota (Rajasthan)	Shriram Chemical Industries
(6)	30	8	Vishakhapatnam (Phase I Expansion) (Andhra Pradesh)	Coromandel Fertilizers Ltd.
	III. Projects under consideration in respect of the establishment of which work may start in the Fourth Plan			
A. Public Sector				
(1)	229	—	Korba (Madhya Pradesh)	Fertilizer Corpn. of India Ltd.
(2)	152	—	Nangal Expansion (Punjab)	-do-
B. Private Sector				
(3)	90	230	Sheva Nhova (Maharashtra)	Dharamsi Morarji Chemicals Company, Bombay
(4)	140	140	Vishakhapatnam (Andhra Pradesh)	Occidental Petroleum Corporation
(5)	125	47	Vishakhapatnam (Phase II Expansion) (Andhra Pradesh)	Vishakhapatnam Fertilizers Ltd.

[*Oil Commentary*, **8** (5) (1970), 19]

TABLE 2—WORLD PRODUCTION OF SULPHUR IN ALL FORMS
('000 tonnes S/S content)

	1967 All-forms	1967 Brimstone	1967 Others	1968 All-forms	1968 Brimstone	1968 Others	1969 All-forms	1969 Brimstone	1969 Others
WORLD TOTAL	34,214	17,896	16,318	36,318	19,799	17,104	38,806	21,134	17,673
Western World	25,806	15,213	10,594	27,489	16,509	10,980	28,506	17,147	11,360
Sub total Communist World	8,407	2,683	5,724	9,414	3,291	6,124	10,300	3,987	6,313
WESTERN EUROPE	7,241	2,056	5,186	7,502	2,108	5,108	7,974	2,208	5,766
Belgium	180	3	177	192	6	186	197	12	188
Cyprus	490	—	490	482	—	482	485	—	485
Finland	364	101	263	411	125	286	490	135	355
France	1,828	1,649	179	1,808	1,623	185	1,895	1,710	185
West Germany	578	106	472	657	127	530	685	135	550
Italy	886	71	815	900	94	806	895	75	820
Norway	318	1	317	356	3	353	444	4	440
Portugal	245	3	242	274	4	270	279	4	275
Spain	1,172	11	1,161	1,228	9	1,219	1,368	3	1,365
Sweden	297	1	296	293	4	289	286	6	280
United Kingdom	520	37	483	521	38	483	555	40	515
Others	365	73	292	380	75	305	395	84	311
AFRICA	542	20	522	534	12	522	562	15	547
Morocco	108	—	108	127	—	127	140	—	140
South Africa	308	8	300	286	9	277	296	11	285
Others	126	12	114	121	3	118	126	4	122
ASIA	2,755	345	2,410	2,964	393	2,571	3,111	488	2,623
India	90	—	90	108	—	108	134	4	130
Iran	16	16	—	21	21	—	80	80	—
Japan	2,533	316	2,217	2,682	336	2,346	2,720	345	2,375
Kuwait	—	—	—	—	—	—	30	30	—
Philippines	73	—	73	87	—	87	90	—	90
Others	43	13	30	66	36	30	57	29	28
OCEANIA	257	10	247	212	11	201	202	12	190
Australia	257	10	247	212	11	201	202	12	190
NORTH AMERICA	12,832	10,692	2,139	14,328	12,194	2,194	14,652	12,517	2,135
Canada	2,972	2,285	687	3,884	3,179	705	4,472	3,847	625
United States	9,860	8,407	1,453	10,444	8,955	1,489	10,180	8,670	1,510
CENTRAL AMERICA	1,979	1,923	56	1,786	1,725	61	1,814	1,752	62
Mexico	1,922	1,896	26	1,729	1,695	36	1,756	1,721	35
Netherlands Antilles	47	21	26	45	22	22	46	23	23
Others	10	6	4	12	8	4	12	8	4
SOUTH AMERICA	201	167	34	165	128	37	192	155	37
Argentina	46	35	11	43	34	99	50	40	40
Bolivia	54	54	—	25	25	—	30	30	—
Chile	60	46	15	38	35	13	54	40	14
Columbia	27	25	2	30	26	4	35	31	4
Others	13	7	6	19	8	11	23	14	9
EAST EUROPE	7,442	2,508	4,934	8,376	3,091	5,286	9,215	3,772	5,443
East Germany	382	123	259	380	120	260	390	125	265
Poland	1,050	800	250	1,591	1,316	275	2,182	1,942	240
U.S.S.R.	5,080	1,550	3,530	5,430	1,600	3,830	5,625	1,650	3,975
Others	930	35	895	976	55	921	1,018	55	963
Other Communist Countries	965	175	790	1,038	200	838	1,085	215	870

[*Monthly Bull. Agril. Econ. and Stats., FAO, Statistical Supplement, No.* 1, March-April **19** (1970), 1]

TABLE 3—ANNUAL STATISTICAL ANALYSIS OF WORLD PHOSPHATE ROCK PRODUCTION AND TRADE
SUMMARY OF WORLD PHOSPHATE ROCK PRODUCTION
[All figures are expressed in thousand tonnes of product]

BY REGION

	1967	1968	1969
TOTAL WORLD	73,775	78,096	77,722
Western World	58,465	61,926	60,847
Communist World	15,310	16,170	16,875
West Europe	87	90	100
East Europe	13,860	14,880	15,375
North America	36,079	37,022	36,000
Central America	176	140	140
Africa	17,040	18,633	18,449
Asia	4,059	4,331	4,670
Australasia	2,253	2,787	2,763

BY PRODUCING COUNTRY

	1967	1968	1969
WEST EUROPE			
France	24	22	30
West Germany	63	68	70
TOTAL	87	90	100
EAST EUROPE			
Poland	100	60	30
U.S.S.R.	13,760	14,820	15,345
TOTAL	13,860	14,880	15,375
NORTH AMERICA			
U.S.A.	36,079	37,022	36,000
TOTAL	36,079	37,022	36,000
CENTRAL AMERICA			
Curacao	114	93	100
Mexico	62	47	50
TOTAL	176	140	150
SOUTH AMERICA			
Brazil	171	150	150
Colombia	—	10	10
Venezuela	50	53	65
TOTAL	221	213	225
AFRICA			
Algeria	180	307	420
Egypt	699	600	600
Morocco	9,922	10,512	10,800
Rhodesia	71	80	80
Senegal	1,266	1,270	1,270
South Africa	942	1,119	1,282
Togo	1,139	1,375	1,470
Tunisia	2,810	3,361	2,500
Uganda	11	9	9
TOTAL	17,040	18,633	18,449
ASIA			
China	1,100	1,000	1,000
Christmas Island	1,091	1,142	1,049
India	15	7	54
Israel	609	730	980
Jordan	894	1,162	980
N. Korea	250	250	300
N. Vietnam	100	40	200
TOTAL	4,059	4,331	4,670
AUSTRALASIA			
Australia	6	5	5
Nauru Island	1,795	2,254	2,193
Ocean Island	452	538	565
TOTAL	2,253	2,787	2,763

[*ibid*, 8]

TABLE 4—SUMMARY OF WORLD PHOSPHATE ROCK IMPORTS AND EXPORTS
[All figures are expressed in thousand tonnes of product]

	1967		1968		1969	
	Imports	Exports	Imports	Exports	Imports	Exports
West Europe	15,668	—	17,545	—	17,143	—
East Europe	4,922	4,600	5,108	6,356	6,356	5,398
North America	2,628	9,306	2,195	10,918	2,478	10,231
Central America	366	143	361	122	135	137
South America	325	—	501	—	392	—
Africa	136	14,081	78	15,549	25	15,234
Asia	4,680	1,371	6,176	1,818	5,850	1,859
Australasia	4,003	3,247	4,601	3,923	3,687	3,807
WORLD	32,748	32,748	37,438	37,438	36,666	36,666

[*ibid*, 8]

TABLE 5—INDIGENOUS PRODUCTION OF PETROLEUM PRODUCTS IN INDIA

	'000 Tonnes		
	1967	1968	1969
Motor Gasolines	1326	1378	1384
Mogas Components	128	53	45
Kerosines Superior	1919	2262	2416
Kerosines Inferior	104	186	122
High Speed Diesel	3024	3287	3629
Light Diesel Oil	877	1003	1090
Furnace Oil	2908	3115	3048
Tea Drier Oil	88	78	84
Low Sulphur Heavy Stock	442	654	919
Hot Heavy Stock	226	215	209
Jute Batching Oil	77	83	61
Bitumen	533	576	690
Lubricating Oil	64	62	100
Liquefied Petroleum Gas	75	100	127
Naphtha	824	937	1214
Petroleum Coke	115	126	150
Wax	36	40	39
Aviation Fuels	489	596	689
Other Products	197	172	223
Total	13452	14923	16239

(Lok Sabha: July 27, 1970)

[*Oil Commentary*, **8** (1) (1970), 15]

TABLE 6—MANUFACTURERS AND INSTALLED CAPACITY OF GRANULATED FERTILIZER MIXTURES IN INDIA

(As on 30th September 1970)

Name of the Factory	Installed Capacity/yr., tons	Date of Production
(I) IN PRODUCTION		
West	392,000	
GUJARAT		
1. Granulated Fertilizers and Feeds Private Ltd., Bhavnagar	50,000	June 1969
MAHARASHTRA	342,000	
1. Dewa Fertilizers and Feeds Ltd., Thana	40,000	Early 1969
2. Kolhapur District Granulated Fertilizers Co-operative Factory Ltd., Gadmudshingi	50,000	March 1969
3. Maharashtra State Co-operative Marketing Federation Ltd., Chikalthana	45,000	Aug. 1970
4. Shetkari Sahakari Sangh Ltd., Rukdi	30,000	April 1968
5. Vidharbha Co-operative Marketing Society Ltd., Badnera	54,000	June 1969
6. Bharat Fertilizer Industries Ltd., Bombay	33,000	April 1964
7. Deccan Sales Corporation, Bhandup, Bombay	45,000	1965
8. Godawari Pravara Canal Co-op. Project & Sales Union Ltd., Kopargaon	45,000@	Before Sept. 1970
North	45,000	
DELHI		
1. D.C.M. Chemical Works, New Delhi	45,000	Sept. 1970
East	30,000	
WEST BENGAL		
1. Phosphate Co., Ltd., Rishra	30,000	Early 1968
Total:	467,000	

TABLE 6—MANUFACTURERS AND INSTALLED CAPACITY OF GRANULATED FERTILIZER MIXTURES IO INDIA (*Contd.*)

Name of the Factory	Installed Capacity/yr., tons	Date of Production	
(II) PLANNED AND YET TO GO INTO PRODUCTION			
South			
ANDHRA PRADESH			
1. Associated Cement Co., Ltd., Kistna (Distt. Guntur)	7.5@ TPH	Feb.	1971
MYSORE			
1. Belgaum Taluka Co-operative Agricultural Produce Marketing Society Ltd., Belgaum	7.5 TPH		1971
2. Chikodi Taluka Agricultural Produce Co-operative Marketing Society Ltd., Khadaklat	7.5 PTH	Feb.	1971
3. Raichur Agricultural Produce Co-operative Marketing Society Ltd., Raichur	45,000	Nov.	1970
TAMIL NADU			
1. Tamil Nadu Co-operative Marketing Federation Ltd., Mannargudi	7.5 TPH		1971
West			
GUJARAT			
1. Associated Cement Co., Ltd., Sevalia (Dist. Khaira)	7.5 TPH@	Feb.	1971
2. Shivrajpur Syndicate Ltd., Shivrajpur	7.5 TPH@	Feb.	1971
MAHARASHTRA			
1. Krishi Organic Chemical Industries Private Ltd., Miraj	50,000	Nov.	1970
2. Maharashtra Agro-Industries Development Co-operation Ltd., Rasayani	90,000*	Nov.	1970
3. Nasik Dist. Co-operative Purchase and Sale Union Ltd., Nasik	7.5 TPH		1971
4. Poona Dist. Co-operative Purchase and Sale Union Ltd., Nimbut	7.5 TPH	Early	1971
North			
PUNJAB			
1. Phosphate Co., Ltd., Rajpura	36,000	March	1971
2. Punjab Fertilizers, Dhandari Kalan	45,000	Oct.	1970
RAJASTHAN			
1. Sri Ganganagar Fertilizer Corporation, Sri Ganganagar	7.5 TPH	March	1971
East			
BIHAR			
1. Bihar State Co-operative Marketing Union Ltd., Patna	30,000		1971
ORISSA			
1. Orissa Co-operative Marketing Society Ltd., Bargarh	7.5 TPH	March	1971

NOTE: TPH: Tonnes per hour
7.5 TPH = 45,000 tonnes per year (approximately)
5.0 TPH = 30,000 tonnes per year (approximately)
@= Provisional. Capacity is expected to vary between 5.0 TPH and 7.5 TPH with the grades produced.
*=Two plants at Rasayani each of capacity 45,000 per annum.

[*FAI Inf. Serv.*, **11** (22) (1970), 13]

TABLE 7—VALUE OF OUTPUT GENERATED IN INDIA BY FOREIGN TECHNICAL COLLABORATION IN 1966-67
(Rs. Crores)

Categories of Companies	No. of Agreements under Foreign Technical Collaboration	Value of Industrial Output by all Companies	Value of Output for Companies with Tech. Collaboration (estimated)
(1)	(2)	(3)	(4)
Subsidiaries (224)	144 (92)	788	502
Minority Capital Participation (367)	445 (259)	770	431
Pure Technical Collaboration (236)	462 (236)	774	774
Total:	1051 (587)	2332	1707

Note: Parentheses in col. 1 give the no. of companies with all types of collaboration. Parentheses in col. 2 give the no. of companies with technical collaboration.

Source: Compiled from Survey Report on Foreign Collaboration in India Industry (1968), Reserve Bank of India.

[*Lok Udyog*, **4** (9) (1970), 1094]

TABLE 8—RESEARCH RATIO* OF INDIA WITH THOSE OF OTHER COUNTRIES

	Research Ratio	R & D Exp. per capita per year ($)	P. C. of R & D Exp. Million ($) to total state	Total R & D Expenditure, (Million $)	R & D Exp. on Manpower to Total Current Expenditure, %
(1)	(2)	(3)	(4)	(5)	(6)
USA[1] (1965)	3.00	105.20	15.4	20470 (6583)	(48.8%)
Japan[2] (1965)	1.36	12.08	3.30	1180 (1167)	(42%) 58.6
Czechoslovakia[3]	N.A.	63.80	3.24	957 (957)	N.A.
W. Germany[4] (1966)	1.80	36.85	2.90	2200 (2010)	(46%) 61.1
India[5] (1968-69)	0.40	0.36	3.20	161 (141)	50-71

* Ratio of Expenditure on R & D to GNP expressed as percentage
N.A.—Not available.

Notes:
1. Figures in brackets in column 1 indicate the reference year.
2. Figures in brackets in column 5 indicate expenditure in civilian research.
3. Figures in brackets in column 6 indicate per cent on total expenditure.

In case of USA it is for the business sector only.

Sources:
1. National Science Policies of USA, 1968, UNESCO & Federal Funds for R. & D and other scientific activities, Vol. XVII. NSF. 68-27.
2. Science Policy & Organisation of Research in Japan, 1967, UNESCO.
3. Science Policy & Organisation of Research in Czechoslovakia Socialist Republic 1965, UNESCO.
4. Science Policy & Organisation of Research in the Federal Republic of Germany, 1969, UNESCO.
5. Report on Science & Technology, 1969, Committee on Science & Technology, Cabinet Secretariat, Govt. of India.

[*Lok Udyog*, **4** (9) (1970), 1089]

TABLE 9—RESERVES OF JHARIA COALFIELD UPTO A DEPTH OF 609 METRES

Seams	Reserve, mill. tonnes
I	407
II	1160
III	698
IV & II/III/IV	1204
V	1058
VI	330
VII	157
V/VI/VII/VIII	1308
VIII	383
VIIIA	226
IX	454
X & IX/X	1284
XI	485
XI/XII	242
XII	381
XIII	520
XIIIA	9
XIIIB	30
XIV	534
XIVA	35
XV	442
XVA	63
XVI	284
XVIA	120
XVII	241
XVIII	111

[*FRI News*, **20** (1) (1970), 11]

TABLE 10—RESERVES OF INDIAN COALS FOR COKING

Particulars	Gross Reserves, (million tonnes)	Extractable Reserves, (million tonnes)
1. Group A Coals		
I. Class 1—Jharia Coalfield		
(A) IX-XVIII seams (less 339 m. of unleased area)	4261	2102
(B) Prospecting Blocks of NCDC* (Kapuria, Monidih, Jarma, Parbatpur, Sudamdih) (less reserves in leased areas of 165 metres)	984	740
II. Class 2-Jharia Coalfield V-VIII-A seam (approx.)	520	260
	5765	3102
2. Group B Coals		
(A) Raniganj Coalfield		
(i) Chanch-Begunia-Ramnagar-Laikdih Seams	769	—
(ii) Shampur-Chatabar basin coals	129	—
	898	478
(B) East Bokaro Coalfield		
(i) Kargali-Kathara-Sawang group and Jarangdih group of seams	2036	1213
(ii) Bermo-Karo group of seams	2011	1168
	4047	2381

TABLE 10—RESERVES OF INDIAN COALS FOR COKING

Particulars	Gross Reserves, (million tonnes)	Extractable Reserves, (million tonnes)
(C) West Bokaro Coalfield* V, VI, VII seams in Loiyo Taping, Kedla Blocks and Ghato area	173	186
(D) Ramgarh Coalfield* VI, VII Top and Bottom and VIII A seam, Block 1	61	30
(E) Kanhan Valley Coalfield* Main seam	100	50
(F) Jharia Coalfield, Raniganj Measures Mohuda group of seams	282	246
Total of Group B coals	5761	3371
3. Group C Coals		
I. Class 1 (Semi-Coking, High Volatile)		
(A) Raniganj Coalfield		
(i) Dishergarh Sanctoria seam	443	239
(ii) Kasta seam (Pariarpur Arang sector)	80	196
(iii) Burra Dhemo-Raghunathbatty-Hatnal seams	270	
(B) Ramgarh Coalfield* VI, VIIA, VII Top and Bottom and VIII seams Block II	178	89
(C) West Bokaro Coalfield* V, VI, VII seams, Pundi Block	121	60
	1092	584
II. Class 2 (Caking, High Volatile)		
(A) Raniganj Coalfield Poniati-Koithee seam	1024	582
(B) Sohagpur Coalfield* V—Seam, Churcha-Jhilimili area	40	20
(C) Jharia Coalfield (Caking, Low Volatile)		
(i) I-I seam	3469	1735
(ii) V-VIIA seam west of Kirkend	1304	652
	6929	3573

NOTE—1. Extractable reserves—after allowing for locked up coals, losses for geological disturbance and mining losses. *Figures taken from various reports of the respective prospecting blocks, etc. For Parbatpur Block, 706 million tonnes up to 800 metres and other blocks up to 600 metres. Other data taken from Coal Assessment Sub-Committee Report 1964.

[*FRI News*, **20** (1) (1970), 12]

TECHNOLOGY Vol. 8 (1971), No. 2, April-June

The following papers Short Communications etc. have been accepted for publication in the next issue of TECHNOLOGY Vol. 8 (1971), No. 2, April-June.

Papers

MECHANISM AND KINETICS OF CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE ON NiO AND NiO—Al_2O_3 SYSTEM
by B. R. Arora, R. K. Banerjee, N. K. Mandal, N. C. Ganguli and S. P. Sen

DEVELOPMENT OF GAS CHROMATOGRAPHIC SUPPORTS FROM SILICA GELS—THEIR COMPARATIVE PERFORMANCE WITH CHROMOSORB—W IN GLC
by N. C. Saha and Samir K. Ghosh

CULTURING ALGAE FOR PRODUCTION OF PROTEIN
by G. S. Bhattacharya, G. S. Roy and B. K. Dutta

POLAROGRAPHIC ESTIMATION OF UREA IN PROCESS LIQUORS
by R. M. Bhatnagar, B. N. Singh and A. K. Roy

X-RAY STUDIES ON NICKEL OXIDE HYDRATES PART 1—HYDRATED PRODUCTS
by C. Aravindakshan, M. Misra and B. K. Banerjee

X-RAY STUDIES ON NICKEL OXIDE HYDRATES PART 2—DEHYDRATED PRODUCTS
by C. Aravindakshan, M. Misra and B. K. Banerjee

A STUDY OF GLAUCONITES FROM CRETACEOUS LIMESTONES OF TIRUCHIRAPALLI AND PONDICHERY
by A. T. Balagopal and K. C. Banerji

A SIMPLIFIED PROCEDURE FOR CALCULATING EQUILIBRIUM COMPOSITION OF GASES OBTAINED FROM REFORMING OF LIQUID HYDROCARBONS
by K. K. Srivastava

EFFICACY OF NITROGENOUS AND PHOSPHATIC FERTILIZERS ON GROWTH AND YIELD OF *Bhindi: (Abelmoschus esculentus L.)*
by N. N. Bid, P. K. Das and S. P. Dhua

CHANGES IN THE MEASURE OF AVAILABLE NITROGEN AND PHOSPHORUS IN ACID SOILS IN PRESENCE OF CALCIUM SALTS
by K. K. Srivastava, Sharafat Ali and S. K. De

EFFECT OF ALTERNATE WETTING AND DRYING ON PHOSPHATE RETENTION
by S. G. Misra and B. P. Gupta

Short Communications.

GRAVIMETRIC ESTIMATION OF CHOLINE BY HEXANITRODIPHENYLAMINE
by J. N. Kapoor and J. M. Sarkar

ATTACK OF AMMONIA SYNTHESIS GAS ON STEELS: CASE STUDIES
by K. M. Verma, H. Ghosh, M. P. Gupta, B. R. Chakravorty, S. C. Verma, V. N. Mishra and A. K. Roy

A STUDY ON THE UREA-MONOCALCIUM PHOSPHATE ADDUCT FORMATION
by S. K. Sengupta and S. Varma

CHARACTERISTICS OF THE RAW WATERS OF HASDEO RIVER AND DHENGUR *Nala* AT KORBA (M.P.)
by G. S. Roy, C. D. Banerjee, G. S. Bhattacharyya and B. K. Dutta

USE OF AQUEOUS STANDARDS FOR ESTIMATION OF IMPURITIES IN WATER-IMMISCIBLE ORGANIC LIQUIDS BY ATOMIC ABSORPTION EMPLOYING DOUBLE CAPILLARY
by K. C. Singhal, R. C. P. Sinha and B. K. Banerjee

DIFFUSION OF CHLORINE ION BY RADIO-TRACER TECHNIQUE
by T. Sahu, I. S. Mishra, S. P. S. Khalsa and S. K. Das

SEDIMENTARY AND DEFORMATIONAL STRUCTURES OF THE KROL FORMATION
by R. Choudhuri and A. T. Balagopal

OXIDATION OF N-BIS (β-AMINOETHYL) DITHIOCARBAMIC ACID WITH ALKALINE FERROCYANIDE
by S. S. Chatterjee

A MODIFIED HIGH TEMPERATURE DILATOMETER FOR STUDYING THE EXPANSION CHARACTERISTICS OF REFRACTORY LININGS AND THERMAL INSULATING MATERIALS
by H. Roy, P. K. Samanta and S. Das

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Vol. 8 APRIL-JUNE 1971 No. 2

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(Continued on next page)

EDITOR: S. N. ROYE
Junior Editors: BENOY K. BANERJEE & S. A. KULKARNI

Cover design by S. K. BASAK

Short Communications

The mechanism and kinetics of hydrogen peroxide decomposition over NiO and $NiO–Al_2O_3$ systems have been studied. It has been shown that rates and mechanism are dependent on the stoichiometry of NiO in the system. While the initial rates of hydrogen peroxide decomposition over catalysts calcined at different temperatures have been found to be proportional to the concentration of Ni^{3+} ions, the overall rates depend on the ratio of concentration of Ni^{3+} and Ni^{2+} in the catalysts and may be related by the empirical equation

$$\text{Log } K_{avg} = \text{Log } a + b \frac{Ni^{3+}}{Ni^{2+}}$$

Mechanism and Kinetics of Catalytic Decomposition of Hydrogen Peroxide on NiO and $NiO\text{-}Al_2O_3$ System

By B. R. Arora, R. K. Banerjee, N. K. Mandal, N. C. Ganguli and S. P. Sen,

Planning & Development Division, Fertilizer Corporation of India Ltd., Sindri, Bihar

Introduction

Nickel oxide is a p-type semi-conductor containing an excess of oxygen and it has been shown that excess oxygen content may be used as a variable to represent the activities, viz. in the oxidation of ammonia[1] and decomposition of hydrogen peroxide on NiO and chromium oxide catalysts[2–5].

Correlation has been obtained by Voltz and Weller[3] and Matsunga[6] for the surface excess oxygen and activity for hydrogen peroxide decomposition over oxidized chromia and chromia-alumina catalysts calcined at different temperatures. The decomposition of hydrogen peroxide over NiO catalyst has been studied by several workers[7–9] and the mechanisms suggested are based on the existence of two oxidation states of nickel forming a reduction potential for the system. A linear relationship between the rate constant of hydrogen peroxide decomposition and the electro-kinetic potential of the catalyst has been found[10].

In the present investigation, the rate of decomposition of hydrogen peroxide over NiO and $NiO\text{-}Al_2O_3$ system has been studied and mechanism and kinetics of the reaction are discussed in relation with excess oxygen in the system forming Ni^{+3} ions.

EXPERIMENTAL

Preparation of Catalyst Samples

Catalyst 1-Nickel Oxide: Nickel carbonate was precipitated from a solution of nickel nitrate and ammonium carbonate. The precipitate was dried and six samples were prepared by decomposing the salt between 410 and 710°C.

Catalyst 2-Nickel Oxide Supported on Alumina: Alumina used as support consisted of α-alumina and was obtained in the extruded form and recalcined at 900°C. The support was soaked in a solution of nickel nitrate and calcined at 400°C. The soaking procedure was repeated to get 8 per cent nickel in the finished catalyst. Seven samples calcined at different temperatures between 350 and 700°C were then prepared.

Catalyst 3-Nickel Oxide Supported on Alumina: Another preparation of catalyst was made by mixing nickel carbonate with calcined powdered alumina. The resultant mass was heated till decomposition of nickel carbonate was complete. Three different samples were obtained by calcination at 450, 560 and 720°C respectively. The finished catalyst contained 8 per cent nickel.

Measurements

1. *Surface Area*: This was measured by the BET, method using nitrogen as adsorbate.

2. *Determination of Excess Oxygen*: The surface excess oxygen was determined by the method described by Uchijima[11], using hydrazine and measuring the nitrogen evolved according to the following reaction.

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2$$

A blank run was made in the case of $NiO-Al_2O_3$ catalysts taking calcined alumina alone and it was ascertained that no nitrogen is evolved due to any reaction taking place between hydrazine and alumina.

3. *Hydrogen Peroxide Decomposition Rates*: A weighed amount of catalyst (about 1 g.) was taken in a reaction vessel placed in a thermostat and connected to a gas collection burette. The amount of oxygen liberated was measured after suitable intervals of time and a blank correction was made in all the experiments. The concentration of hydrogen peroxide used was 0.2 M.

Results and Discussion

The results of excess oxygen, surface area, etc. are given in Tables 1-3.

For hydrogen peroxide decomposition rates, Figs. 1-3 give the plots of oxygen liberated vs. time for various catalysts. The values for initial and average rates of hydrogen peroxide decomposition (Tables 1-3) are obtained from Figs. 1-3, which represents the oxygen liberated after 1 min. and mean values obtained by dividing the oxygen liberated with successive intervals of time, respectively.

The surface area and excess oxygen decrease with the increasing temperatures of calcination for pure NiO and supported $NiO-Al_2O_3$ (catalyst 3), while for $NiO-Al_2O_3$ (catalyst 2) a maximum value is observed both for the surface area and excess oxygen at 560°C. This phenomena has been attributed to the preparation method of this catalyst and possible reasons for this are discussed

TABLE 1—CATALYST 1

Calcination Temperature, °C	Surface Area, M^2/g	Excess Oxygen, At %	No. of Ni^{3+} Ions/g.	$\frac{Ni^{3+}}{Ni^{2+}}$ Ratio	Initial Rates for H_2O_2 Decomposition, Ki c.c./min.g.	Average Rate Kavg. c.c./min.g.
410	84.86	2.03	3.27×10^{20}	42.27×10^{-3}	3.53	3.3
450	53.51	1.29	2.03×10^{20}	25.83×10^{-3}	2.20	1.35
520	22.18	0.65	1.05×10^{19}	13.19×10^{-3}	1.06	0.63
560	13.19	0.44	7.10×10^{19}	8.87×10^{-3}	0.80	0.43
620	10.07	0.29	4.68×10^{19}	5.84×10^{-3}	0.50	0.37
710	7.2	0.20	3.22×10^{19}	4.01×10^{-3}	0.40	0.31

TABLE 2—CATALYST 2

Calcination Temperature, °C	Surface Area, M^2/g	Excess Oxygen, At %	No. of Ni^{3+} Ions/g.	$\frac{Ni^{3+}}{Ni^{2+}}$ Ratio	Initial Rates for H_2O_2 Decomposition, Ki c.c./min.g.	Average Rate Kava. c.c./min.g.
350	18.35	0.23	3.66×10^{19}	60.15×10^{-3}	0.20	0.17
420	16.10	0.24	3.87×10^{19}	63.81×10^{-3}	0.22	0.19
500	15.01	0.25	4.09×10^{19}	67.70×10^{-3}	0.235	0.22
560	19.54	0.29	4.52×10^{19}	75.34×10^{-3}	0.26	0.25
600	19.05	0.28	3.66×10^{19}	60.15×10^{-3}	0.20	0.18
650	17.02	0.19	3.12×10^{19}	50.83×10^{-3}	0.18	0.13
700	14.40	0.13	2.15×10^{19}	34.47×10^{-3}	0.12	0.088

TABLE 3—CATALYST 3

Calcination Temperature, °C	Surface Area, M^2/g	Excess Oxygen, At %	No. of Ni^{3+} Ions/g.	$\frac{Ni^{3+}}{Ni^{2+}}$ Ratio	Initial Rates for H_2O_2 Decomposition, Ki c.c./min.g.	Average Rate Kava. c.c./min.g.
450	47.98	0.28	4.52×10^{19}	75.34×10^{-3}	0.48	0.38
560	45.72	0.24	3.81×10^{19}	62.76×10^{-3}	0.42	0.26
720	43.80	0.22	3.53×10^{19}	57.89×10^{-3}	0.36	0.22

in another communication[12] on the problem of excess oxygen in supported $NiO-Al_2O_3$ catalyst.

The data for Ni^{3+} ions given in tables are obtained from the excess oxygen, assuming that one excess oxygen atom corresponds to two Ni^{3+} ions[13]. The ratio Ni^{3+}/NI^{2+} is calculated from the number of Ni^{3+} ions as obtained above and from the No. of Ni^{2+} atoms which is equal to $\frac{6.023 \times 10^{23}}{74.7}$ per g. of nickel oxide.

Kinetics and Mechanism of Hydrogen Peroxide Decomposition Over Pure NiO: Beg and Ghosh[14] have shown that the order of reaction for decomposition of hydrogen peroxide over hydrous nickel oxide varies with the concentration of peroxide. They have considered the reaction to be of zero order when 0.147 M hydrogen peroxide is used, and with dilute peroxide the reaction changes to first, second and third orders with the degree of dilution.

In the present experiments, 0.2 M hydrogen peroxide was used and the reaction is expected to be of zero order so that a plot of oxygen liberated against time should be a straight line. From Figs. 1-3 it can be seen that the rates are not exactly of zero order and the deviation increases as the calcination temperature of the catalyst increases.

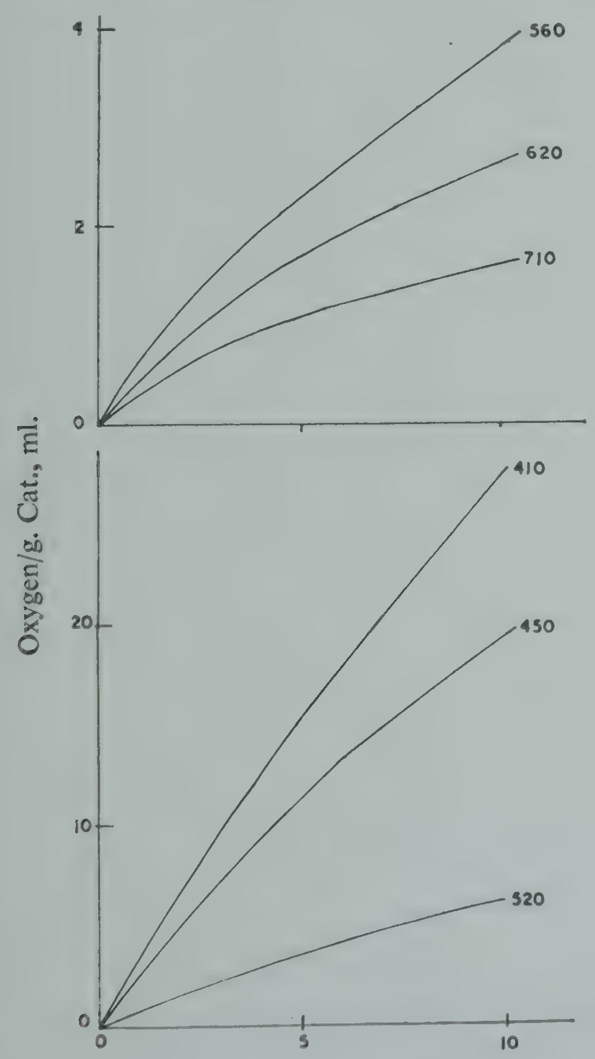


Fig. 1—Hydrogen Peroxide Decomposition Rates Using Catalyst 1

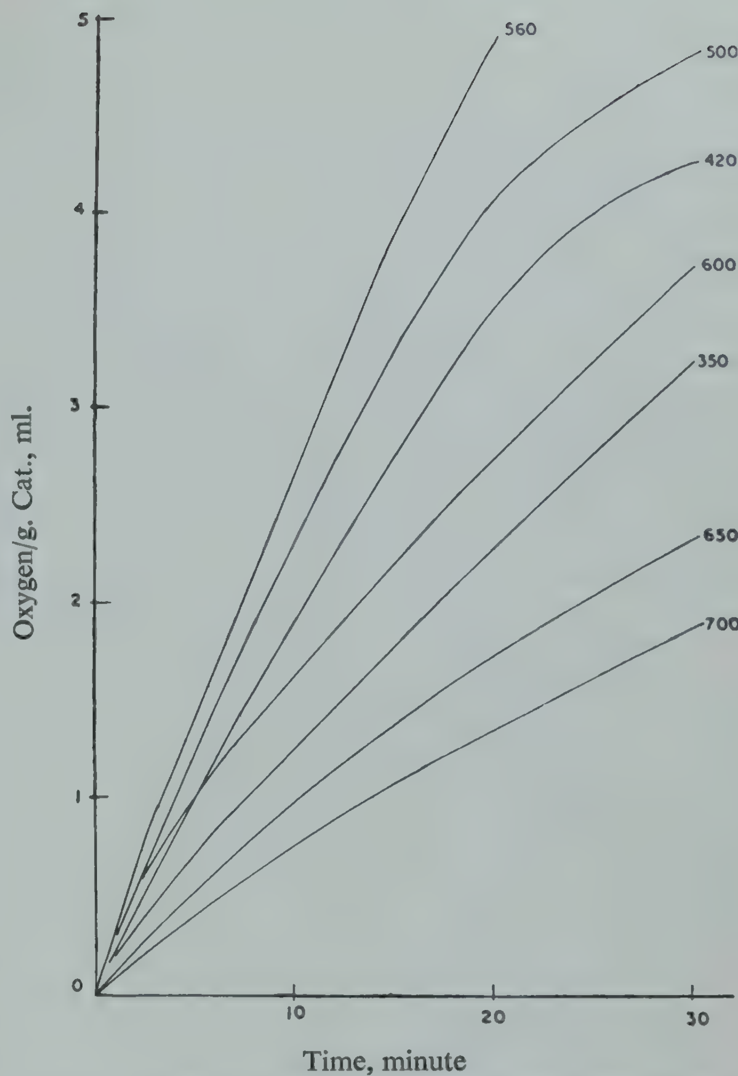


Fig. 2—Hydrogen Peroxide Decomposition Rates Using Catalyst 2

Roy[8] has discussed the mechanism of decomposition of H_2O_2 on oxide systems on the basis of standard reduction potential of such systems. He has considered that in NiO and Ni_2O_3, the standard reduction potentials of such system (M^{n+}/M or $M^{(n+1)+}/M^{n+}$) are lower than the corresponding values of $O_2\ 2H^+/H_2O_2$, so that it is likely that hydrogen peroxide will be reduced primarily in presence of such system

$$H_2O_2 + e \rightarrow OH + \overline{OH}$$

The electrons will be available from element (M) as

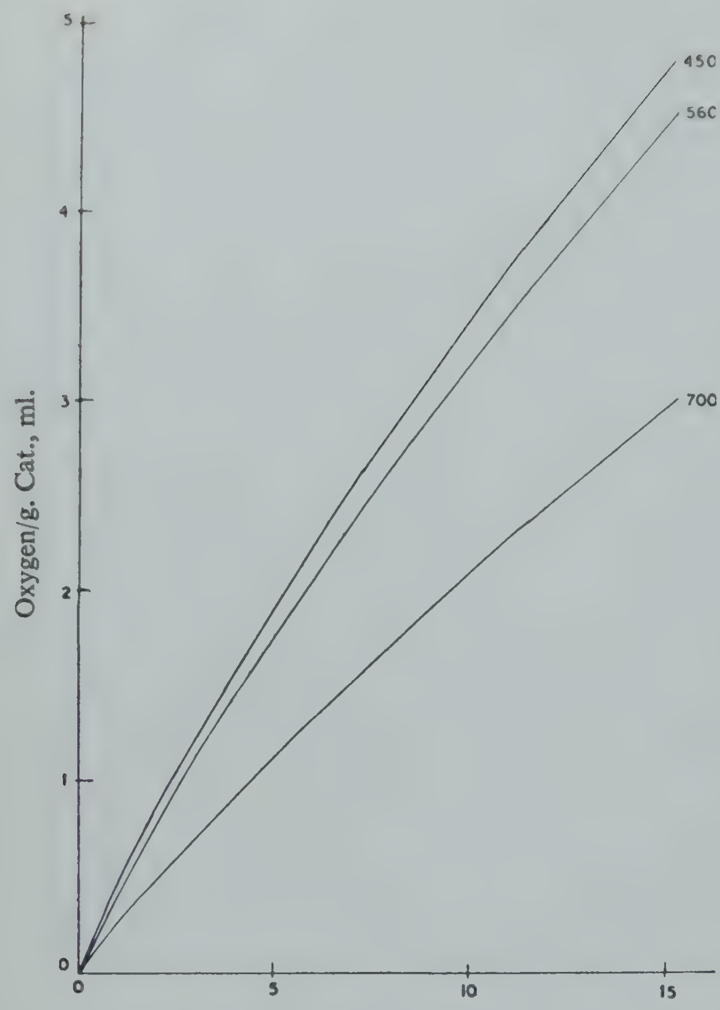
$$M \rightarrow M^{n+} + ne$$

$$\text{and/or } M^{n+} \rightarrow M^{(n+1)+} + e$$

On the basis of Haber and Weiss mechanism[15], the chain reaction may be terminated by the local excess of M^{n+} ions which will react with free radical OH as

$$M^{n+} + OH \rightarrow M^{(n+1)+} + \overline{OH}$$

Richardson[16] has explained the semi-conducting pro-



Time, minute
Fig. 3—Hydrogen Peroxide Decomposition Rates Using Catalyst 3

perties in non-stoichometric nickel oxide due to the existence of Ni^{3+} in conjunction with Ni^{2+} and the conduction mechanism through the holes jumping from Ni^{3+} to Ni^{2+} sites. It is obvious therefore that Ni^{3+} sites, with an affinity for accepting electron, when placed in contact with hydrogen peroxide are likely to initiate the reaction. The initial reaction of hydrogen peroxide decomposition over non-stoichometric NiO may begin with the acceptance of electron by the Ni^{3+} sites

$$\text{i.e. } Ni^{3+} + e \rightarrow Ni^{2+}$$

The above reaction clearly involves the oxidation of hydrogen peroxide and this is in contradiction with the assumption of Roy[8] who has considered that the reaction between Ni_2O_3 and hydrogen peroxide will be primarily that of reduction of hydrogen peroxide.

The above conclusion is also supported from the consideration of redox potential of these systems. The values for standard reduction potential NiO system are given in Table 4.[17]

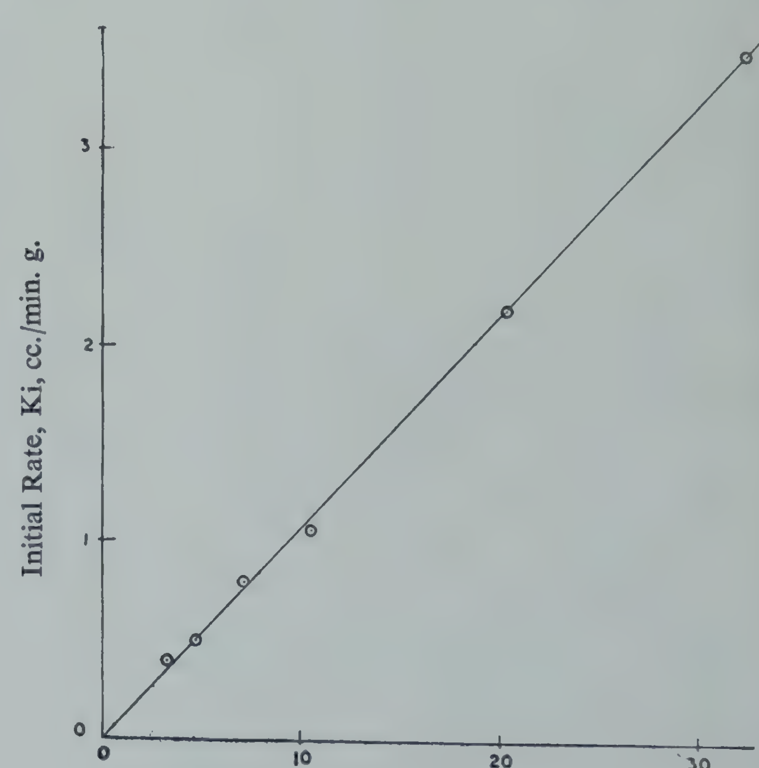
Since the standard reduction potential of Ni^{2+}/Ni (stoichiometric NiO) is less than that of O_2, $2H^+/H_2O_2$, the

TABLE 4

Redox System	Standard Reduction Potential
NiO_2/Ni^{2+}	1.75
Ni^{2+}/Ni	−0.25
O_2, $2H^+/H_2O_2$	0.682

H_2O_2 may be primarily reduced. For the redox system Ni_2O_3/Ni^{2+} the data for the standard reduction potential is not available but for NiO_2/Ni^{2+} the value is much higher than O_2, $2H^+/H_2O_2$ and hence the reacton with hydrogen peroxide in this case should start with the oxidation of hydrogen peroxide. For Ni_2O_3/Ni^{2+} system which mainly constitutes the nickel oxide calcined at least in the range of 400-600°C the value could be assumed less than that of NiO_2/Ni^{2+} but it should be higher than that for hydrogen peroxide, so that even for Ni_2O_3/Ni^{2+} system the oxidation of hydrogen peroxide should be the reaction.

If it is true that oxidation of hydrogen peroxide by Ni^{3+} is the primary mechanism, the initial rates of decomposition will be governed by the concentration of Ni^{3+} ions in the catalyst. In Figs. 4 and 5, the initial rates (Ki) are plotted for the various catalysts against the number of Ni^{3+} ions and a straight line is obtained, which confirms that at least the initial reaction takes



No. of Ni^{3+} Ions $\times$ 10^{19}
Fig. 4—Dependence of Initial Rates on Ni^{3+} Concentration in Catalyst 1

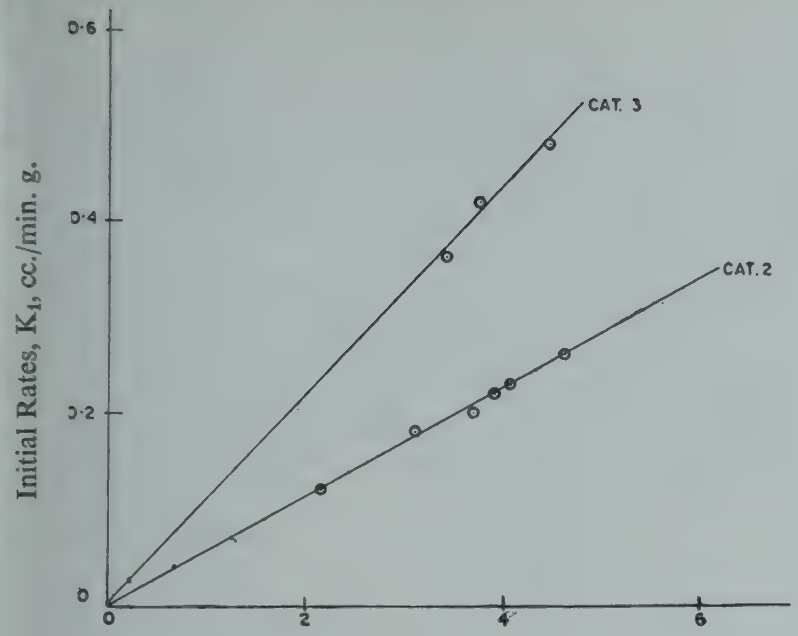


Fig. 5—Dependence of Initial Rates on Ni^{3+} Concentration in Catalysts 2 and 3

place between the Ni^{3+} and hydrogen peroxide which is through the oxidation of hydrogen peroxide.

The mechanism could thus be outlined.

$$Ni^{3+} + H_2O_2 \rightarrow Ni^{2+} + HO_2 + H^+$$

The radical HO_2 formed in the first electron transfer will initiate the decomposition reaction as follows:

$$HO_2 + H_2O_2 \rightarrow HO + O_2 + H^+$$
$$HO + H_2O_2 \rightarrow HO_2 + H_2O$$

The chain reaction will be terminated by the reaction of HO with Ni^{2+}

$$X.\ Ni^{2+} + (HO)_y \rightarrow Ni^{2+}{}_x\ HO_y$$

The samples calcined at lower temperature have large excess of Ni^{3+} ion and hence rates will be faster than in the samples calcined at higher temperature which have comparatively less Ni^{3+} ions. This is confirmed from experiments, which shows the decreasing rates of hydrogen peroxide decomposition with increasing temperature of calcination.

For the stoichiometric NiO, however, the mechanism[14] may be different and reaction may proceed through

$$X\ Ni^{2+} + Y\ H_2O_2 = Ni^{2+}{}_x\ (HO\text{-}OH)_y$$
$$= Ni^{2+}{}_x\ OH_y + Y\ OH$$

The radical OH thus produced will initiate the chain reactions of decomposition of hydrogen peroxide, and then there may be a number of chain-breaking reactions the significant one being

$$X\ Ni^{2+} + (OH)_y = Ni^{2+}{}_x\ OH_y$$

Thus, it is to be concluded that rates and mechanism o decomposition of hydrogen peroxide is different for non-stoichiometric and stoichiometric NiO and in one case it is the oxidation of hydrogen peroxide controlled by concentration of Ni^{3+} ions and in other it may be reduction of hydrogen peroxide as proposed by Roy[8], controlled by the concentration of Ni^{2+} ions.

The average rates of decomposition could be proportional to the ratio Ni^{3+}/Ni^{2+} ions.

This has been experimentally found to be true and a plot of Log K_{avg} against Ni^{3+}/Ni^{2+} yields a straight line (Figs. 6 & 7), which leads to an empirical relationship between the average rate of decomposition K_{avg} and $\frac{N^{3+}}{Ni^{2+}}$ as

$$\text{Log}\ K_{avg} = \text{Log}\ a + b\left(\frac{Ni^{3+}}{Ni^{2+}}\right)$$

where a and b are the constants depending on the method of preparation. This, in fact, also explains the deviation in Figs 1-3, since as the raction proceeds the ratio of

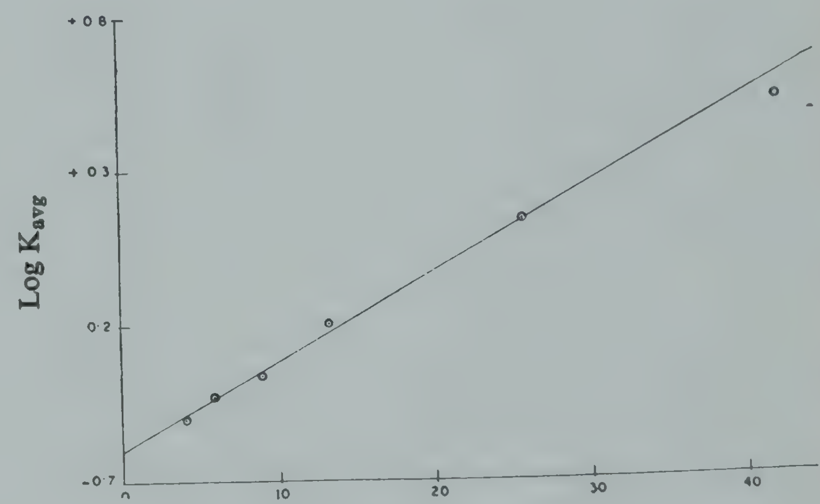


Fig. 6—Relation between Average Rates and Ni^{3+}/Ni^{2+} Ratio in Catalyst 1

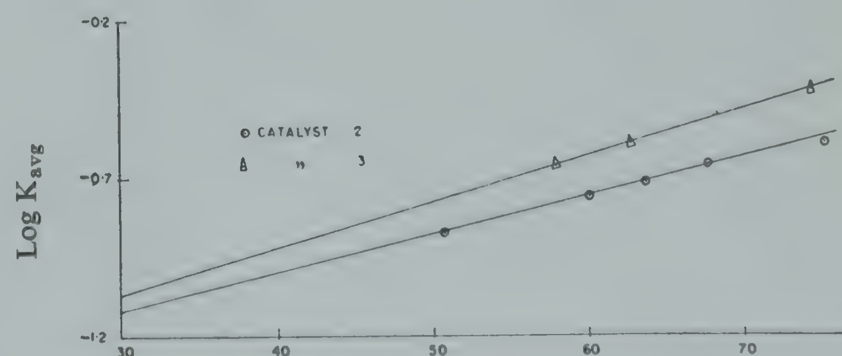


Fig. 7—Relationship between Average Rates and Ni^{3+}/Ni^{2+} in Catalysts 2 and 3

Ni^{3+}/Ni^{2+} changes, and so changes the mechanism through which reaction with hydrogen peroxide is taking place.

Nickel-Alumina Catalysts: The results of catalyst 1 and 3 indicate that presence of alumina modifies the properties of catalyst 3 in such a manner that the extent of decrease in surface area and excess oxygen with increase in calcination temperature is less pronounced. However, there exists similarity between these two catalysts in the nature of changes of these parameters. But the catalyst 2, which is also preparation of NiO on alumina like catalyst 3, exhibits certain distinct characteristics. Unlike other two catalysts, its surface area and excess oxygen initially increase with increase of temperature of treatment and after reaching maximum at 560°C steadily decreases. This difference in behaviour between the catalyst 2 and 3, both of which are alumina-supported and having same nickel content may be attributed to the difference in state of dispersion of nickel caused by variation in the method of incorporation of nickel. It has also been observed that with this particular catalyst (No. 2) increase in excess oxygen content is accompanied with a higher rate of decomposition of hydrogen peroxide. This indicates dependence of catalytic activity on surface excess oxygen, i.e. Ni^{3+} concentration, and therefore lends further support to the relationships proposed by us.

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A number of supports for GC work having different pore size distributions have been developed from inexpensive and indigenous silica gels by salt-thermal treatment. A representative one with the largest average pore diameter has been critically examined for physical properties and elution characteristics against Chromosorb-W for its suitability as GLC column packing material. The high thermal efficiency of the modified silica (MS) will be a distinct advantage in large scale GC. The MS has permeability and specific retention volume, which are about half of those of Chromsorb-W when supports containing equal amount of stationary liquid are run under identical conditons, but peak separation factors are comparable. $\bar{H}$ vs $\bar{U}$ characteristics are some what inferior in MS, which is associated with its narrower and deeper pores. Nevertheless, the resolution of adjacent peaks is superior in MS.

For microscale comparison of GLC supports, some extended concepts of retention index, such as I-T linearity rule, have been applied for the first time. I-T plots gave correct indication of secondary effects (other than those originating from the properties of the bulk stationary liquids) for different types of solutes in MS. For those solutes which were found free of support effects, retention indices are similar in the two supports; moreover, these solutes are eluted with cent per cent recovery from MS and their quantitative analysis is as good as in Chromosorb-W.

Development of Gas Chromatographic Supports from Silica Gels—Their Comparative Performance With Chromosorb-W in GLC

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The performance of a gas chromatographic support is ultimately related to the parameters of pore geometry and surface chemistry. For example, the contributions to the theoretical plate in both the mobile and stationary phases are predominantly controlled by the pore geometry of the support[1,2]. Chemistry of the surface affects peak symmetry, retention volume and resolution in GLC to a certain extent. It has been established by the present authors in earlier publications[3–6] that the geometry of pores and chemistry of surface of silica gels can be suitably modified by a combination of physical and chemical treatments to generate a series of supports with different pore size distributions for the gas-solid chromatography of various types of compounds, especially the hydrocarbons. The details of the process will be covered in a patent. In the present study, one of the modified silicas with the largest average pore diameter was chosen and examined for suitability in gas-liquid chromatography work. Since the diatomaceous types of supports, particularly the Chromosorb-W, is the almost universal GLC support, the performance of the modified silica has been necessarily compared with the former. Mention may be made that these modified silica supports are many times cheaper than the Chromosorbs and, additionally, in certain difficult separations the residual activity of the silicas may be advantageously utilized. For example, a mixture of 1, 2 butadiene, cyclobutene and acetone was not separated in 10 per cent squalane on Chromosorb-W, but were completely resolved in 10 per cent squalane on MS.

Experimental

Physical properties of the supports were determined by the conventional methods. Comparison of column efficiency was based on an accurate determination of the more reliable system of Kovats index[7] in preference to relative retention of solutes and on still finer basis on the recently found rule of variation of retention index with column temperature. The gas chromatograph used was an Aerograph Hy Fi 600D with a flame ionization

detector. Necessary precautions were taken to maintain proper control of carrier flow and oven temperature. For the determination of retention index the solute was always injected along with its two corresponding normal paraffins and data averaged from triplicate runs. Squalane and tricresyl phosphate (B.D.H.) and XE-60 (Applied Science Corpn.) were used, the amount being 10 w/w per cent. The columns were made from 1/8″ copper tubing after proper cleaning and drying. Liquid loading capacity was determined by stepwise addition of squalane with mild stirring on 1 g. of support till lumping and coalescing tendency, i.e. loss of free-flowing property, was observed.

Results and Discussion

1. Mechanical Strength

The modified silica support was sieved to -60, $+72$ mesh (B.S.S.) and packed into a $5' \times 1/4''$ column which was then subjected to 80 psig. inlet pressure at 225°C for 5 hr., the carrier flow at outlet being 120 ml./min. The contents after cooling gave the sieve analysis as in Table 1.

TABLE 1—Mechanical Strength of Modified Silica under Gas Chromatographic Conditions

(Sieve Analysis of $-60 + 72$ mesh MS after use in a $5' \times \frac{1}{4}''$; column at 225°C, and 80 psig for 5 hr.

Mesh Range, BSS	Amount, W%
−60, + 72	94.5
−72, + 80	4.5
−80, + 100	0.3
−100, + 120	0.7

No fines above 120 mesh were obtained. The resultant fines were actually 1 per cent i.e. of miesh size -80 to $+120$, part of which might have resulted during packing and unpacking of the column. Thus, the mechanical strength of the MS under GC operating conditions is fairly good.

2. Physical Properties

The physical characteristics of MS was compared with Chromosorb-W in Table 2. The Na_2CO_3-calcined Chromosorb-W has alkaline pH while the transition metal salt fired MS shows slightly acidic pH. The salt-thermal treatment has imparted to the hygroscopic silica gel a strong water-repellent property much better than Chromosorb-W. This property will give a longer life to GLC columns packed with MS particularly with moisture-sensitive stationary liquids. A comparison of bulk density and specific surface area indicates a scope for further improvement of the salt-thermal process, particularly for the analysis of bigger molecules. The capacity for liquid phase is somewhat better for the MS compared to acid-washed and silanized Chromosorb-W of similar particle size range.

TABLE 2—Physical Properties of Modified Silica and Chromosorb-W

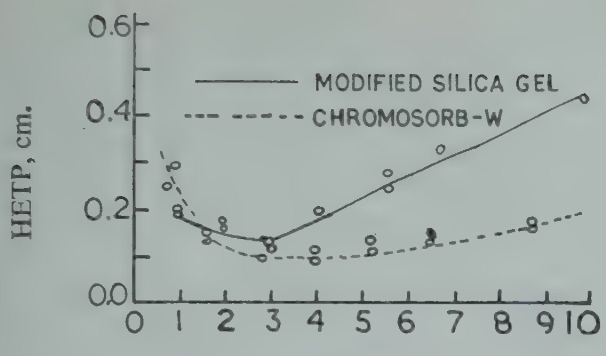
	Modified Silica	Chromosorb-W
Color	Black	White
pH	6.3 −7.5	8−10
Bulk Density, g/cc	0.61−0.83	0.24
Moisture, %	0.1	1
Surface Area BET, m²/g.	24−30	1−3.5
Liquid Loading Capacity, w/w%	30−45	30

A remarkable property of the MS is its high thermal conductivity due to incorporation upto about 10 per cent of metal. Thus, MS can be advantageously utilized in preparative and industrial scale GC separations. The thermal lag during the elution of front and back of a band[8] will be quickly dissipated by MS, while the conventional GC supports are virtually thermal-insulators.

3. Comparison of Elution Characteristics

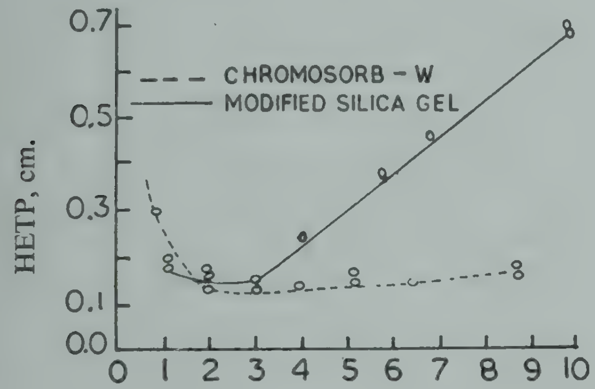
(a) *Permeability*: Gas hold-up determined from methane retention was 1.5 ml. for the $10' \times 1/8''$—10 per cent XE-60 on MS at 140°C and the corresponding value for the Chromosorb-W column was 2.4 ml., particle size in both cases being 60/80 mesh. Apparatus dead-volume was roughly estimated as 0.7 ml.; hence, the actual free space for gas transport per g. of coated support in MS and Chromsorb-W columns are 0.8 and 1.7 ml. respectively. In other words, the permeability of Chromosorb-W is double that of MS.

(b) *Plate Efficiency*: The height equivalent to a theoretical plate (H) was determined for n-butyl acetate in Fig. 1 and for normal nonane in Fig. 2 from columns $10' \times 1/8''$—10 per cent XE-60 on the two supports at 140°C for various linear velocities of argon-carrier gas. These $\bar{H}$ values were not corrected for apparatus dead volume and zero sample size. The amount of sample injected was always 0.1 microlitre liquid. Plate height is a good measure of the nonequilibrium band broadening processes and column efficiency. In other words, $\bar{H}$ determines the suitability of the structure of supports in GLC. Comparing $\bar{H}$ vs $\bar{U}$ curves in Figs. 1 and 2, it is noted that the $\bar{H}_{min}$. value is higher and its $\bar{U}$ range for



u, cm/sec.

Fig. 1—Plot of $\bar{H}$ vs $\bar{U}$ for n-Butyl Acetate at 140°C from 10 × ⅛″ Columns Containing 10 % w/w XE-60 on Chromosorb—W and on MS



u, cm/sec.

Fig. 2—Plot of $\bar{H}$ vs $\bar{U}$ for n-Nonane at 140°C from the same Two Columns as in Fig. 1

approximately constant $\bar{H}_{min}$. is fairly narrow for the modified silica than the high efficiency Chromosorb-W. Therefore, considerable scope is there for the modification of pore parameters of the MS which is being actively pursued in this laboratory. For example, silanization will definitely improve the quality of MS. An ideal support should have fairly wide, uniform and shallow pores to generate isolated pools as thin films of stationary liquid in order to permit very rapid mass transport of solutes. Another disadvantage of the MS is related with the rapid rise of $\bar{H}$ with $\bar{U}$ which exposes its relative inefficiency for high speed GLC work.

(c) *Relative Retention*: Comparing the corrected retention volumes in XE-60, it is noted from Table 3 that the value in MS is about 1.8 times greater than in Chromosorb-W for different types of hydrocarbons. Considering the fact that specific retention volume in GLC is contributed by solubility as well as adsorption of solute on the stationary liquid[9], it is understandable that the additional contribution in the MS column must have stemmed from its having 10 to 25 times higher surface area than Chromosorb-W. Peaks were, however, symmetrical in both columns. An important and basic implication of this finding is that the retention volume is also controlled by support parameters in GLC. It has been established

TABLE 3—Comparison of Retention Volumes in Modified Silica and Chromosorb-W

Solute	10′×1/8″—10% XE-60 on MS at 140°C		10′×1/8″—10% XE-60 on Chromosorb-W at 140°C	
	Retention Volume/g. Phase	Retention Volume/g. Support	Retention Volume/g. Phase	Retention Volume/g. Support
Normal nonane	35.7	3.6	19.7	2.0
1 trans 2-Dimethyl cyclohexane	29.6	3.0	17.3	1.7
Toluene	45.2	4.5	27.5	2.7

by Saha and Giddings[10] that stationary liquid when coated on a support assumes the configuration of its pores. Since the pores in MS are much narrower and deeper compared to those of Chromosorb-W, it is possible that the rate of capture and release of solute from pools of stationary liquid in the former is about 1.8 times slower than in the latter support. It is also evident from steeper rise of $\bar{H}$ vs $\bar{U}$ plot in MS than Chromosorb-W in Fig. 1. Only scattered evidences of the difference in Vg of a solute in supports of different pore geometry are available in literature[11,12], and hence the precise contributions of different pore parameters towards Vg should await systematic research.

(d) *Peak Separation*: The ratio of the distances of centres of two bands in GLC is independent of pore geometry of the support. But the surface characteristics of the support which when interacts significantly with the eluting solutes and/or stationary liquid—can alter the relative retention data. It is noted from Table 4 that the separation factors of adjacent peaks of different hydrocarbons are essentially the same on 10 per cent XE-60 on both MS and Chromosorb-W, thereby indicating that

TABLE 4—Comparison of Peak Separation Ratios of Some Hydrocarbons in Modified Silica and Chromosorb-W

Solute	Separation Factor at 140°C From 10′×1/8″—10% XE-60 on MS	10′×1/8″—10% XE-60 on Chromosorb-W
Benzene–toluene	1.62	1.70
Toluene–*p*-xylene	1.60	1.59
p-Xylene–*o*-xylene	1.22	1.24
1 *cis* 2-Dimethyl Cyclohexane–*n*-nonane	1.20	1.23
n-Nonane–toluene	1.26	1.30

TABLE 5—COMPARISON OF RESOLUTION OF HYDROCARBONS AT 140°C FROM XE-60 COLUMNS

System	Chromosorb-W		MS	
	Resolution R	$\frac{R}{(t_1+t_2)/2}$	Resolution R	$\frac{R}{(t_1+t_2)/2}$
Benzene–toluene	2.73	0.70	4.01	0.76
Toluene–*p*-xylene	3.05	0.66	3.79	0.51
p-Xylene–*o*-xylene	1.85	0.31	3.53	0.36
nN—IT2 DMCH	0.36	0.10	1.33	0.27
uN—Toluene	1.54	0.38	1.94	0.34

t_1 is the retention time in min. of the first hydrocarbon and t_2 of the second.

MS is equally inert as Chromosorb-W at least so far as hydrocarbons are concerned.

(e) *Resolution of Peaks*: It has already been discussed that a peak is retained much longer and is much wider in MS than in Chromosorb-W. Nevertheless, it has been observed in Table 5 that the resolution of adjacent peaks determined under the conditions for $\bar{H}_{min}$ region is remarkably better in the former support. It is not clear why the resolution per unit of time is slower in the MS for some separations but faster for others, as compared with Chromosorb-W.

(f) *Retention Indices*: Much more refined and definite test of the chemical intertness of a support surface is the comparison of retention or arithmetic indices and their variation with column temperature. Three stationary liquids of different polarity, viz. squalane, tricresyl phosphate (TCP) and XE-60 were coated in 10 per cent on MS and Chromosorb-W, which was acid washed and silanized. Column temperatures are given in Table 6. Kovats retention indices (I) were determined as usual by injecting the solutes and the corresponding normal paraffin pair in the sequence of their elution order and the results are given in Table 6. It can be noted that the discrepancy in the retention indices of all types of hydrocarbons for these stationary liquids is within 4 units or less between modified support and Chromosrob-W. Mention may be made here that considering the instrumental and other limitations, such as shortness of column length, inaccuracy in oven temperature (not better than 2°C) and carrier flow, the present authors do not claim better than ± 2 units of accuracy in the index values of Table 6. Moreover, had MS been silinized also, the basis of comparison would be at par and better agreement in results could be expected. It is, therefore, concluded that MS is as inert as Chromosorb-W towards all hydrocarbons at least. Ketones also do not show significant interaction

TABLE 6—EFFECT OF SUPPORT ACTIVITY ON THE RETENTION INDEX OF SOLUTES IN GLC

SOLUTE	Retention Indices in					
	10%—XE-60 at 80°C		10% TCP at 100°C		10% Squalane at 86°6	
	Modified silica	Chromosorb—W	Modified silica	Chromosorb—W	Modified silica	Chromosorb—W
Diethyl Ether	576	578	586	582	—	—
Disoprophyl Ether	648	650	650	646	—	—
Hexene-2	653	654	648	644	608	606
224 TMP	690	687	682	679	694	694
Cyclo Hexane	708	711	706	708	669	672
Cyclo Hexene	753	757	758	758	682	681
234 TMP	768	766	759	759	—	—
235 TMP	779	778	764	761	—	—
Acetone	760	763	715	716	678	434
Methanol	698	712	735	768	—	—
Ethanol	737	747	—	—	—	—
Ethyl Acetate	792	800	766	754	539	557
Benzene	822	826	816	820	652	469
IC 2 DMCH	874	873	—	884	—	—
IT 2 DMCH	837	839	850	847	—	—
Propanol	847	851	890	829	—	—
E. M. Ketone	858	862	799	795	—	—
Toluene	924	928	920	925	—	—

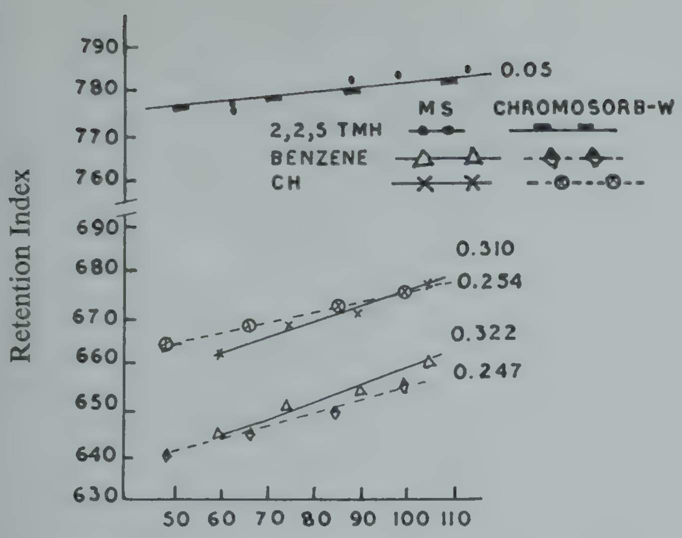


Fig. 3—Linearity of Retention Index with Temperature from 10% w/w Squalane on Chromosorb-W and on MS

[The slope values are given at the right hand side of each line]

with MS when coated with polar liquids like XE-60 or TCP, but show a very strong interaction on non-polar solvents, like squalane. Alcohols and esters were found to interact appreciably on MS when coated with stationary liquids of any polarity. This is particularly observed in first few members, but rapidly fades out as alkyl radical size increases in the molecule.

(g) *Index-Temperature Rule*: It has been established by Saha and Mitra[13,14] that retention index varies strictly linearly with column temperature irrespective of the nature of solutes and solvents, carrier flow rates and practical range of column temperature employed. If the support is active and actually interacts with solute molecules presumably through absorption, then the latter force may give a different mode of variation with column temperature and will have a I-T linear plot with different slope and intereept than the corresponding column with an inert support or in extreme cases may even deviate from the I-T linearity rule. I-T plots in the two supports coated with squalane in Fig. 3 for a few representative hydrocarbons, viz. 2, 2, 5 trimethyl hexane (TMH) for the saturated and cyclohexane (CH) for cyclic and benzene for aromatic hydrocarbons. It is noted from Fig. 3 that saturated paraffins have identical I-T plot in the two supports, i.e. they do not have undesirable support effects. On the contrary, cyclic and aromatic hydrocarbons show small secondary suppoɪt effect as evidenced in the small variation of slope of the still linear I-T plots. The slope values were given at the right hand side of each plot. This effect has been magnified in polar solutes in Table 7 where temperature co-

TABLE 7—Effect of Support Activity on the Temperature Co-efficient of Retention Index in GLC

Solute	ΔI/10°C	
	MS—10% XE-60	Chromosorb-W—10% XE-60
225 TMH	2.20	3.14
Ethyl Methyl Ketone	5.83	6.69
Benzene	3.68	6.89

efficients of all types of hydrocarbons are significantly lowered in MS compared to its blank Chromosorb-W. However, a definite statement on the difference of temperature coefficient of retention index is only possible when two methods of determination of I are much more precise than is claimed in this paper.

4. Recovery of Solutes and Quantitative Analysis

A support used for quantitative GLC work must give symmetric peaks, cent per cent recovery of solutes and must not cause any chemical transformation of samples. The MS support used as GLC columns has been found to be free from peak asymmetry and artifact peaks. In order to test quantitative elution a synthetic mixture of hexene-2, ethyl acetate, methyl ethyl ketone and toluene were analysed on XE-60 coated on MS and its blank Chromosorb-W. All the components were completely resolved on both supports. Peak areas were calculated from peak height times half-width, response factors

TABLE 8—Comparison of Quantitative Elution Among Chromosorb-W and Modified Silica Gel Supports

Solute w/w %	10% XE-60 on Chromosorb-W			10% XE-60 on MS			Deviation, %
	1st set	2nd set	Average	1st set	2nd set	Average	
Hexene-2	25.4	26.6	26.0	25.4	24.5	24.9	−4.0
Ethyl Acetate	7.7	8.3	8.0	7.9	8.4	8.2	+1.9
E. M. Ketone	25.8	25.2	25.5	24.2	25.6	24.9	−2.4
Toluene	41.1	39.9	40.5	42.5	41.5	42.0	+3.7

were assumed equal for these solutes in the FID, and individual percentages were found from summated peak areas. Sample size was 0.1 microlitre injected by a 1 microliter Hamilton syringe. An analysis of results reveals no appreciable variation from support to support as compared with one run to another. Moreover, the deviation in results of MS from those in Chromosorb-W are within experimental limits, considering the limited precautions which could be maintained. In other words, MS permits quantitative equation of solutes with the exception perhaps of alcohols and certain heterocyclic compounds.

Conclusion

By salt-thermal treatment of silica gel, satisfactory supports for non-polar solutes have been economically prepared in this laboratory. Further refinements of the process are under way for tailor-making pore geometry and surface chemistry to generate a series of well-defined GLC supports for efficient and optimum resolution of compounds of various polarity and molecular dimensions.

A great need was felt for application of sophisticated and powerful GC and other techniques to identify and quantitate secondary effects, i.e. those not associated with properties of stationary liquids, giving rise to poor reproducibility of retention data and recovery of solutes

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The technical feasibility of protein production through culture of a highly proteinaceous strain of unicellula algae was studied under the local climatic conditions using a semi-continuous bench-scale culture apparatus. *Chlorella*, a fast growing unicellular green alga with high contents of proteins, vitamins and minerals, was grown in the apparatus under outside weather conditions throughout a year utilizing an inorganic growth medium and carbon dioxide enriched air. The algal strain showed positive growth all round the year irrespective of climatic conditions. A maximum yield of about 10 g. dry wt/m^2/day and a minimum of about 6.0 g. dry wt/m^2/day were observed in April and December respectively, the average yield (dry weight) of the year being 8.0 g/m^2/day corresponding to about 12 metric tonnes dry wt/acre/yr. as compared to 1.5 tons dry weight of average field crop in most agricultural areas.

Culturing Algae for Production of Protein

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Introduction

Of the important food constituents, viz. carbohydrate, protein and fat, proteins are in shortest supply, though more than half of the world's cultivated and pasture land is presently being utilized to produce the essential proteins[1].

The conventional proteinaceous foodstuffs like meat, fish, egg and milk, are produced at a very low photosynthetic efficiency resulting in a very low yield of protein and high cost. It has been shown[2] that the annual protein production/acre of land for conventional animal proteins, like milk and meat, are 90 and 54 lbs respectively in striking contrast to 14,000 lbs for *Chlorella* protein. From cost factor too, the algal protein should be cheaper as photosynthetic efficiency achieved in algal protein formation is much higher than even most of the vegetable proteins. Studies with algal protein[3–6] have revealed that the nutritive value of *Chlorella* protein is surprisingly high, being comparable or even superior to that of dried skim milk or egg white. All the essential amino-acids required for mammalian nutrition except methionine[7], are present in the above protein in adequate amounts. *Chlorella's* food value is further enhanced by its high content of essential vitamins and minerals[3,7].

Though considerable interest has been shown in algal protein in recent years in various parts of the world,[8–12] no attempt has so far been made in this country towards its production through large-scale algal culture in spite of ready availability of its raw materials and favourable weather conditions.

It was felt by the present authors that the conventional methods of protein production had failed to cope with its ever-increasing demand by the increasing population of India and the protein supply position was bound to be more acute in days to come. Investigations were, therefore, made on the technical feasibility of production of an algal protein and estimating its food and feed values.

Studies were made on the nutritional requirements and growth characteristics of algae because any evaluation of algae as organisms potentially useful for converting solar energy into a protein-rich algal protoplasm must include consideration of their growth requirements and characteristics. Laboratory studies with batch and continuous cultures had yielded much useful information about suitable algal species, growth medium, carbon-dioxide requirement, growth rate, harvesting and yield of algae[13,14]. The present paper deals with a bench-scale semi-continuous culturing technique of algae developed in the laboratory and discusses the growth and yield of *Chlorella*, a unicellular protein-rich green alga, at various seasons of the year under the natural climatic conditions met in this part of the country.

Materials and Method

Culture Apparatus: The bench-scale culture apparatus (Fig. 1) consisted of three 22 cm. diam. narrow mouth clear glass bottles, with proper fittings for carbon dioxide

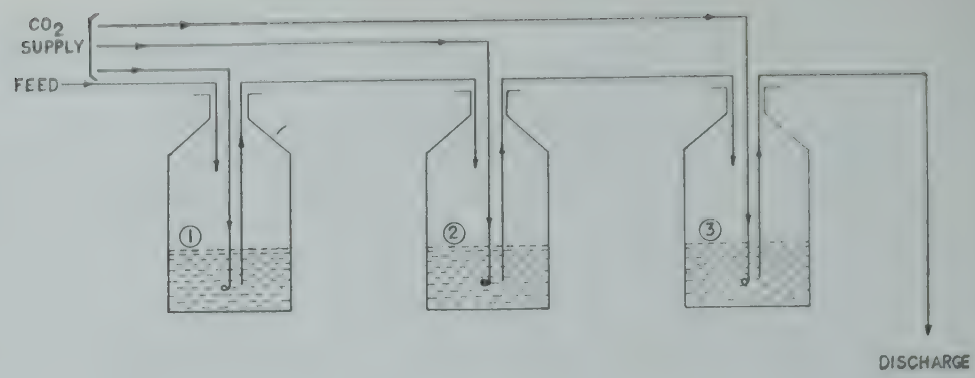

Fig. 1—Schematic Diagram of the Bench-Scale Chlorella Culture Apparatus

diffusion, as containers of the culture. The bottles were numbered 1, 2 and 3 and arranged in series. Each container had 10 lit. of culture, giving a total culture volume of 30 lit. in the apparatus. The total illuminated surface of the apparatus was 0.65 m^2. The apparatus was set up on a suitable wooden platform, built just outside the laboratory window, to enable the algal culture to grow under natural climatic conditions. The three containers served in principle the same purposes as the three compartments of a multi-compartmental outdoor culture tank. In the semi-continuous operation of the culture apparatus, a certain volume of the algal culture, containing high concentration of algal mass, was periodically discharged from the third container for harvesting; an equal volume of the fresh growth medium was fed into the first container. Inside the apparatus, the culture was made to flow from container 1 to 3 via 2 (Fig. 1).

Growth Medium: The growth medium used for precultures was prepared by dissolving suitable amount of algal nutrients in tap water and had the following composition:

Item	Concentration, mg./1.
Urea	320
K_2HPO_4	170
$Ca(HCO_3)_2$	128
$Mg(HCO_3)_2$	90
$(NH_4)_2SO_4$	40
$FeSO_4.7H_2O$	2.00
$ZnSO_4.7H_2O$	0.44
$CuSO_4.5H_2O$	0.08
$Co(NO_3)_2.6H_2O$	0.10
$(NH_4)_6Mo_7O_{24}.4H_2O$	0.04
$MnSO_4.H_2O$	0.03
H_3BO_3	1.00

The medium for semi-continuous bench-scale culture, though containing adequate amounts of all the aforesaid algal nutrients, was prepared in a somewhat different manner. All the nutrients were not dissolved together in the tap water for preparing the growth medium. The main feed entering into the container 1 consisted of 320 mg./1. of urea prepared with tap water, the latter contributing sufficient calcium, magnesium and sulphate ions to the medium. The required doses of potassium phosphate and trace elements were fed separately to each container from stock solutions of these substances prepared for the purpose. This technique of growth medium preparation minimized the chances of loss of phosphate and trace elements from the system by precipitation and helped as well to maintain the concentration of trace elements in the medium below their toxic level.

The stock potassium phosphate solution contained 44.8 g. of K_2HPO_4/1. of distilled water. The stock solution of trace elements was prepared by dissolving 0.440 g. $ZnSO_4.7H_2O$, 0.080 g. $CuSO_4.5H_2O$, 0.100 g. $Co(NO_3)_2.6H_2O$, 0.040 g. $(NH_4)_6Mo_7O_{24}.4H_2O$, and 0.030 g. $MnSO_4.H_2O$ in 100 ml. of 1 per cent boric acid solution. Iron—another essential trace element—was not added to this stock solution for its tendency to precipitate out. It was added to each of the containers from a working ferrous sulphate solution prepared fresh before use by dissolving 0.250 g. $FeSO_4.7H_2O$ in 100 ml. of distilled water.

5-6 ml. each of stock potassium phosphate and ferrous sulphate solution and 0.1-0.2 ml. of stock trace element solution were dosed separately to each of the containers after the daily schedule of discharge and feed was over.

Carbon Dioxide Supply: In addition to the elements classed as macro- and micro-nutrients constituting the growth medium, a third element, carbon, must be supplied to the medium as gaseous carbon dioxide to obtain a culture of a high population density. 10 per cent carbon dioxide in air, prepared by proper dilution of the byproduct carbon dioxide from an ammonia factory, was

bubbled to the culture for 8 hours/day, from 8 A.M. to 4 P.M. at an average rate of 5 ml./min./1. of culture. The by-product carbon dioxide had the following percentage composition (v/v): CO_2 80.0, H_2 10.0, CO 1.6, O_2 0.4, CH_4 0.4, and N_2 and other inert gases 7.6. Apart from providing adequate carbon to the growth medium carbon dioxide diffusion controlled the pH of the culture to the proper level and helped to provide some amount of culture mixing.

Culture Mixing: The mixing or agitation, which is so essential for proper light and nutrient utilization of a continuous culture, was achieved primarily by carbon dioxide bubbling. In addition to this continuous agitation, vigorous mixing for 2-3 min. at intervals of 2-3 hr. during the day time was provided to the culture by bubbling compressed air. This helped to keep the algal cells in proper suspension and prevented them from settling at the bottom and adhering to the walls of the containers.

Algal Inoculum: The alga used as inoculum belonged to the same *Chlorella* species as was used in previous studies[14]. It was a protein-rich, fast-growing, hardy and unicellular green alga capable of showing positive growth under a wide range of fluctuating chemical and physical environment.

Operation of the Culture Apparatus: Each of the three containers of the culture apparatus was filled to the 10 l. mark with the growth medium given earlier for pre-cultures and started carbon dioxide diffusion through the medium immediately afterwards. Each container was then inoculated with about 200 mg. (as dry weight) of the centrifuged and washed *Chlorella* cells obtained from the cultures maintained in the laboratory. The cultures were allowed to grow under batch process till they attained a density of 1.2-1.3, expressed as optical density, or 1200-1300 mg/1 expressed in terms of dry weight of cells. At this stage the apparatus was switched over from batch process to semi-continuous operation by resorting to daily discharge and feed schedule as given below.

5 l. of culture were discharged from the third container to which was transferred equal volume of culture from the second container. The second container was, in turn, fed by 5 l. of culture from the first container. Finally, 5 l. of fresh growth medium was fed in the first container. All the above steps of discharge, culture transfer and feed were carried out manually once every morning. Day-to-day growth of the cultures was followed by determining the optical densities and dry weight of cells per unit volume of the culture[13]. Phosphate, nitrogen, alkalinity and pH of the cultures were also estimated daily to check their level in the culture medium, particularly that of the last container. It was observed that the cultures, under the semi-continous technique of operation, attained a steady-state condition as regards nutrient level, algal density, alkalinity and pH by—7-8 days after start and maintained this state for months together in absence of any abrupt change of environmental condition or contamination by microanimals such as protozoa or rotifers.

Environmental Conditions: The cultures were exposed to outdoor weather conditions throughout the entire course of this study. Solar radiation, incident day-light intensity and day temperature varied over a wide range both diurnally and seasonally. Visible solar radiation was found to be minimum (110-165 g. cal/cm^2/day) in December-January, and maximum (190-288 g. cal/cm^2/day) in May-June. The incident day-light intensity varied from 150-6500 ft. candles in December-January to 250-11,000 ft. candles in May-June. The cultures received direct sunlight for 5-7 hr. out of 11-13.5 total sunshine hours, the rest of the day it came under the shade of the laboratory building.* The maximum temperature was attained by the cultures in the afternoons of hot summer days of April-June (45-47°C) and minimum temperature was reached in the morning hours of cold days of December-January (12-15°C).

Harvesting and Drying of Algae: The finely dispersed *Chlorella* cells were recovered from the daily outflow of the culture apparatus either by centrifugation or by alum flocculation. 5 min. of centrifugation at 3000 rpm were found to be sufficient for recovering almost all the *Chlorella* cells from the culture solution. The centrifuged algal mass was washed with water, oven-dried at 100-103°C, crushed and ground to a fine powder and finally stored in sealed bags. For recovering the *Chlorella* cells by alum flocculation about 100-150 mg/1 of alum was required to properly flocculate the cells from a culture containing 0.12 to 0.15 per cent of dry algal solids depending upon the alkalinity and pH of the culture. The optimum pH range for alum flocculation was found to be 5.5-6.0 The flocculated algal mass was filtered under suction through filter cloth, washed and dried as usual.

Results and Discussion

The average growth rate and yield of dried *Chlorella* cells attained in the culture apparatus in different months

*This, invariably, has put some limitations on the growth and yield of algae in the culture apparatus. The productivity of the apparatus would have further enhanced if the cultures received direct sunlight for more sunshine hours of the day.

TABLE 1—GROWTH AND YIELD OF *Chlorella* IN THE SEMI-CONTINUOUS BENCH-SCALE APPARATUS IN DIFFERENT MONTHS

Month	Days of Operation, no.	Culture Temperature, °C		Solar Radiation (visible), g. cal/cm²/day		Average Growth Rate, g./l/day	Average Daily Yield of Dried Algae, g./m²/day
		Minimum	Maximum	Minimum	Maximum		
January 1968	31	16	33	117	170	0.137	6.3
February „	28	20	43	127	203	0.204	9.4
March „	27	24	43	159	238	0.210	9.7
April „	27	25	46	165	269	0.220	10.1
May „	20	23	46	192	287	0.195	9.0
June „	19	23	47	154	288	0.154	7.1
July „	18	28	39	174	286	0.162	7.5
August „	17	27	41	175	273	0.134	6.2
September „	16	26	40	167	246	0.158	8.8
October „	17	25	43	139	220	0.201	9.3
November „	28	21	40	123	179	0.195	9.0
December „	31	15	36	105	166	0.130	6.0

of the year together with the culture temperature and solar radiation for each month are given in Table 1. It is evident that the *Chlorella* strain showed positive growth throughout the year irrespective of local climatic conditions. The highest growth rate and maximum yield were, however, observed in April (growth rate, 0.220 g/1/day and yield, 10. g/m²/day) whereas lowest growth rate and minimum yield were noticed in December (growth rate, 0.130 g/l/day and yield, 6.0 g/m²/day). In the monsoon months (July-September) the sky remained cloudy/overcast for about 50 per cent of the days, which hampered the algal growth and resulted in comparatively poor yield. The average daily yield for the year was calculated to be about 8.2 g/m²/day corresponding to about 12.14 tonnes dry wt/acre/year as compared to 1.5 metric tonnes dry-weight of average field crop in most agricultural areas. In terms of protein, the production figure of algal protein would come to about 7.4 metric tonnes per acre per year as compared to only 54 lbs/acre/year for milk protein and 90 lbs/acre/year for meat protein.

Table 2 gives the average chemical composition of oven-dried *Chlorella* and pure protein. It is indicated from these data that nitrogen content of dried *Chlorella* is 55-65 per cent of that of pure protein. In case the nitrogen content of the algae is converted to crude protein by following the standard practice[15,16] using the factor of 6.25 the crude protein content in algae would come to about 61 per cent as compared to 35.6 per cent in dried skim milk and 55-70 per cent in fish meal.

The amino acids and vitamin assays of *Chlorella* have been adapted from other workers[3,18] (Tables 3 and 4) in order to highlight the richness of *Chlorella* protein.

Summary and Conclusion

The technical feasibility of production of algal protein through large-scale culture of *Chlorella* was studied under

TABLE 2—AVERAGE CHEMICAL COMPOSITION OF DRIED *Chlorella* AND PROTEINS

Item	Concentration, % by wt.	
	Dried *Chlorella*	Proteins[17]
Carbon	52.0	51-55
Hydrogen	7.4	6.5-7.3
Oxygen	27.9	20-24
Nitrogen	9.8	15-18
Phosphorus	0.9	0-1.0
Sulphur	0.4	0-2.5

TABLE 3—CONTENTS OF AMINO ACIDS IN DRIED *Chlorella* (Adapted from Hayami, H., Matsuno, Y. and Shino[18], K)

Amino Acids	Contents, g./100 g. dry matter		
	Simple Freeze-dried	Blanched	Methanol-treated
Isoleucine	2.22	2.07	2.28
Leucine	5.28	5.15	5.88
Lysine	4.28	3.58	4.44
Phenylalanine	3.15	2.78	3.27
Threonine	3.0	2.65	3.18
Methionine	0.95	0.91	1.08
Valine	3.83	3.18	3.39
Histidine	0.95	0.84	1.15
Arginine	4.25	3.91	4.23
Tryptophane	0.95	0.92	1.07

TABLE 4—ASSAY OF VITAMINS IN DRIED *Chlorella* (Adapted from Combs[3], G.F.)

Vitamin	Concentration
Vitamin C, mg./kg.	600
Carotene, mg./lb.	218
Thiamin, mg./lb.	4.5
Riboflavin, mg./lb.	16.3
Niacin, mg./lb.	109.0
Pyridoxine, mg./lb.	10.4
Pantothenic acid, mg./lb.	9.1
Choline, mg./lb.	1370.0
Biotin, μg./lb.	67.0
Vitamin B 12, μg./lb.	10.0
Vitamin K, mg./kg.	6.0

the various climatic conditions met in this part of the country using an outdoor, semi-continuous, bench-scale culture apparatus and a synthetic inorganic growth medium having proper arrangements for diffusion of diluted carbon dioxide through it. The inorganic nutrients of the aqueous growth medium reacted with carbon dioxide in presence solar energy to form protein-rich *Chlorella* cells. The growth rate and yield of *Chlorella* varied with the seasonal fluctuations in environmental conditions and were maximum in summer and minimum in winter months, the yields of the rainy months falling in-between. The average daily algal yield for the year under study was 8.2 g. dry wt/m^2/day, corresponding to about 12.14 metric tonnes dry wt/acre/year or about 7.4 tonnes/acre/year as algal protein. It is obvious, therefore, that per acre yield of protein from algal source would be much higher than those of proteins from conventional sources. Considering the rich food values of algal protein this high productivity figure is very much encouraging.

From the aspects of yield and nutritive value algal culture for protein production seems to be a technically feasible project under the local conditions and deserves further study on a bigger scale to evaluate its economic feasibility.

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The polarographic method of estimating urea[1] has been modified and then applied to determine urea content of various process streams of an urea plant. A reversible wave of Ti^{4+} has been obtained in 0.4N sulphuric acid + 0.3M ammonium sulphate + 0.2M urea base electrolyte, with a single electron reduction of Ti^{4+} to Ti^{3+}. The wave has been found to be unaffected by biuret.

Polarographic Estimation of Urea in Process Liquors

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Introduction

Urea has been found[1] to affect the limiting current of Ti^{4+} in ammonium sulphate + sulphuric acid base electrolyte and this property has been utilized for its estimation. The method of estimation as such could not, however, be applied to process liquors in urea plant containing carbon dioxide, ammonia and biuret because of the formation of excess ammonium sulphate during neutralization, which affects the titanium wave. The procedure has, therefore, been further modified and applied to various process liquors containing urea. The results of the study are reported in this paper.

Experimental

Polarograms were recorded on a LP-60* self-recording polarograph with dropping mercury electrode. The glass capillary with $m^{2/3}t^{1/6} = 1.68$ at the height 31 cm. was used throughout. All studies were carried out in a H type Novak cell[2]. To effect deaeration, nitrogen was bubbled through the cell for 15 min. before each experiment. All the polarographic studies were carried out at 30°C. Stock solution of titanum was prepared from AnalaR potassium titanyl oxalate as given by Vogel[4]. Samples of various process liquors were collected from different points of FCI's Sindri and Gorakhpur urea plants at ordinary temperatures. All the chemicals used in the present work were of AnalaR quality.

Effect of Urea on Behaviour of Ti^{4+} in Sulphuric Acid-Ammonium Sulphate Base Electrolyte: Titanium solution was taken in a 100 ml volumetric flask, to which calculated quantities of sulphuric acid, ammonium sulphate and urea were added so that the solution in the flask had 0.005M Ti^{4+}, 0.4N sulphuric acid, 0.3M ammonium sulphate and 0.2M urea. The polarograms were recorded (Fig. 1).

Effect of Ammonium Sulphate on the Behaviour of Ti^{4+} in Urea-Sulphuric Acid Base Electrolyte: Solutions were prepared, as indicated in the previous paragraph, which after dilution to the mark had the following composition 0.005M Ti^{4+}, 0.4N H_2SO_4, 0.2M urea and 0 to 2M ammonium sulphate. Polarograms were recorded and the results are presented in Table 2.

Effect of Biuret: Urea containing 0 to 2 per cent biuret was taken and solutions were prepared as above which after making up had 0.005M Ti^{4+}, 0.4N sulphuric acid

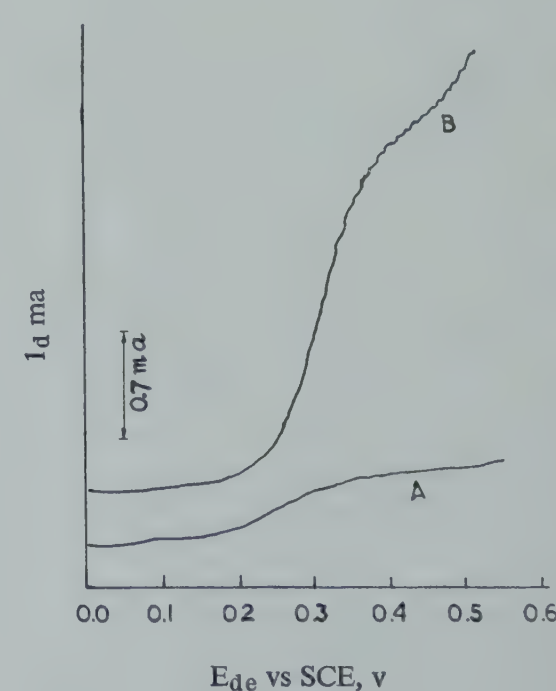


Fig. 1

*Kovo Instruments Co., Czechoslovakia.

TABLE 1—VALUES OF i_d, $E_{1/2}$, I AND SLOPE OF Ti^{4+}

Base Electrolyte	i_d, ma.	$E_{1/2}$ vs SCE, volt	I	Slope	Nature
(a) 5m M Ti^{4+} + 0.4N H_2SO_4 + 0.3 M $(NH_4)_2SO_4$	0.29	−0.26	0.03	0.059	Reversible
(b) 5m M Ti-+ + 0.4 N H_2SO_4 + 0.3 M $(NH_4)_2SO_4$ + 0.2 M Urea	1.85	−0.31	0.22	0.061	Reversible

TABLE 2—EFFECT OF AMMONIUM SULPHATE ON THE POLAROGRAPHIC BEHAVIOUR OF Ti^{4+} IN A BASE ELECTROLYTE, Ti^{4+} 5mM SULPHURIC ACID 0.4N

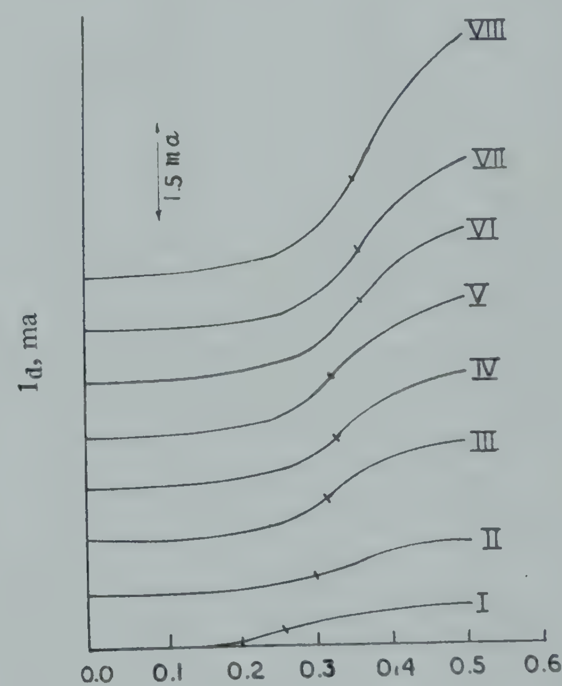
Concn. of $(NH_4)_2SO_4$, M	$E_{\frac{1}{2}}$ vs SCE, Volt.	i_d ma,	I
1. 0.0	− 0.26	1.12	0.13
2. 0.25	− 0.26	1.12	0.17
3. 0.50	− 0.31	1.15	0.14
4. 1.00	− 0.33	1.03	0.12
5. 1.50	− 0.34	0.83	0.10
6. 2.00	− 0.35	0.72	0.08

ammonium sulphate 0.3M and 0.2M urea with varying amounts of biuret. Polarograms were recorded.

Calibration of the Working Graph: In a series of 100 ml volumetric flasks, calculated quantities of titanium solution, sulphuric acid, ammonium sulphate and urea ranging from 0 to 1.75 g. were added; the solution after dilution to the mark had 0.005M Ti^{4+}, 0.4N sulphuric acid, 0.3M ammonium sulphate and different amounts of urea. Polarogram of each solution was recorded (Fig. 2). Diffusion currents were calculated and plotted against urea concentrations (Table 3).

The following procedure was adopted to remove carbon dioxide and ammonia of process liquors and for the estimation of urea. A typical analysis of the recycle liquor in a urea plant operated by the FCI is as follows: At the inlet—NH_3 = 39.80 CO_2-29.32, H_2O 21.40, urea 9.26 and biuret 0.22 per cent temp. 100°C and at the outlet—urea 30.25, NH_3 35.75 CO_2 14.85, H_2O 18.99 and biuret 0.06 per cent; temp. 185°C.

About 5 g. of the liquor containing urea, carbon dioxide ammonia and biuret was taken in a 250 ml beaker and heated for about 30-45 min. on a water-bath below 90°C. The content of the beaker was then transferred to a 100 ml. volumetric flask and diluted to the mark. 25 ml. of this solution was taken in a 100 ml. volumetric flask to which titanium, sulphuric acid and ammonium sulphate solutions were added. The polarograms were recorded and urea content was found out from the calibration graph. Various synthetic mixtures with known amounts of urea, carbon dioxide ammonia were prepared and treated as above and urea content was estimated polarographically. Polarographic results were further compared with those obtained by the standard Kjeldahl digestion method[3] using selenium



E_{de} vs SCE, v

Fig. 2

TABLE 3—VARIATION OF DIFFUSION CURRENT OF Ti^{4+} WITH UREA CONCENTRATION (CALIBRATION CURVE)

(Base electrolyte—H_2SO_4—0.4N, $(NH_4)_2SO_4$—0.3M and Ti^{4+}—0.005M)

Amount of Urea/ 100 ml., g.	Concn, of Urea, moles/l.	i_d, ma.
0.0	0.000	0.28
0.25	0.042	0.56
0.50	0.083	0.88
0.75	0.125	1.18
1.00	0.166	1.46
1.25	0.208	1.75
1.50	0.250	2.04
1.75	0.291	2.10

metal and copper sulphate as catalyst (Table 4). The results of analysis of various process liquors are given in Table 5.

Results and Discussion

Polarograms of Ti^{4+} in 0.4N sulphuric acid and 0.3M ammonium sulphate as base electrolyte with and without urea are reproduced in Fig. 1. The values of i_d, $E\frac{1}{2}$, I and slope are given in Table 1. The plot of log i/i_{d-i} against E_{de} for each curve has been found to be linear with slope 0.059 (Fig. 1A) and 0.061 (Fig. 1B), the value of n has been calculated from the slope and found to be unity in each case. This shows that the system is reversible and confirms one electron reduction of Ti^{4+} to Ti^{3+} according to equation.

$$Ti^{4+} + e^- \rightarrow Ti^{3+}$$

From Fig. 1, it is clear that urea definitely affects the polarographic behaviour of Ti^{4+} in the base electrolyte mentioned above. The increase in the diffusion current (i_d) is about six times with 0.2M urea, with a shift in $E\frac{1}{2}$ from 0.26 to 0.31 volt (Fig. 2). This change may be due to a complex formation, studies on which will be published in a subsequent paper.

The plot of urea concentration against diffusion current (i_d) has been found to be linear (Table 3) upto 0.30M urea and this working graph has been used to estimate urea in the process liquors polarographically.

Ammonium sulphate is formed during the neutralization of the recycled liquor, so the effect of various amounts of ammonium sulphate was studied on the polographic behaviour of Ti^{4+} in a sulphuric acid-urea base electrolyte. From Table 2, it is clear that the diffusion current of Ti^{4+} is very much affected by the presence of varying amounts of ammonium sulphate. Initially, it increases rather than decreases with the increase of ammonium sulphate concentration. The value of $E\frac{1}{2}$ has also been found to shift to more negative potential. This effect may also be due to complexing which requires a detailed study. So, it was found necessary to remove ammonia and carbon dioxide from the process liquors to their minimum level before estimating urea polarographically.

The process liquors of urea plant contain varying amount of biuret, formation of which depends on the conditions of manufacture. The effect of biuret upto 2 per cent with respect to urea has been studied. The diffusion current (i_d) 1.27 ma, has been found to be uneffected by the presence of varying amounts of biuret in urea (upto 2 per cent).

In order to confirm the present method, various synthetic mixtures with different amounts of urea, carbondioxide, ammonia, biuret and water contents were prepared. Their urea content was estimated polarographically after removing carbon dioxide and ammonia. The results are presented in Table 4. The results of polarographic analysis were further confirmed by the Kjeldahl digestion method. The average standard deviation has been calculated from at least six estimations and found to be 0.01.

TABLE 4—ESTIMATION OF UREA IN KNOWN SYNTHETIC MIXTURES CONTAINING UREA, AMMONIA AND CARBON DIOXIDE

(Base electrolyte —Ti^{4+}5mM, $H_2SO_4$0.4N and $(NH_4)_2SO_4$ 0.3M.

Mixture Consists of	Urea by Digestion Method, g.	Urea by Polarographic Method, g.	Standard* Deviation
Urea alone	0.403	0.410	0.01
,,	0.305	0.304	0.00
,,	0.700	0.700	0.01
,,	0.620	0.616	0.01
,,	0.850	0.844	0.01
			Mean Standard Deviation 0.01
Urea + NH_3 +CO_2+Biuret	2.46	2.47	0.02
,,	1.80	1.81	0.01
,,	1.41	1.40	0.01
,,	3.00	3.00	0.01
,,	2.00	2.02	0.01
			Mean Standard Deviation 0.01

+Standard deviation calculated from 6 estimations.

TABLE 5—ESTIMATION OF UREA IN VARIOUS PROCESS LIQUORS OF UREA PLANTS AT GORAKHPUR AND SINDRI

(5 g. of the sample taken)

Sample	Source & Date of Collection	Urea by Digestion Method, %	Urea by Polarographic Method, %	% Error
C_1	Sindri reactor (1.2.69)	56.10	56.70	+ 1.07
C_2	,,	51.40	50.80	− 1.17
S_1	,, (8.2.69)	53.67	54.36	+ 1.30
S_2	,,	81.40	80.55	− 1.05
AC/C	Gorakhpur reactor (19.3.69)	43.48	44.13	+ 0.8
AC/D	,,	50.02	50.24	+ 0.8
HD_1	Gorakhpur decomposer (19.3.69)	54.32	54.00	+ 0.59
HD_2	,,	67.20	66.72	− 0.70

The results of analysis of urea contents of various process liquors collected from different points of urea plants at Sindri and Gorakhpur units of FCI are presented in Table 5. The individual errors of samples were calculated—taking the Kjeldahl digestion method values as standard—and found to be ± 1.5 per cent.

Conclusion

The present polarographic method can be used to determine urea in various process liquors of urea plants. It is quick and accurate.

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Some of the nickel oxide hydrates obtained by oxidation of alkaline divalent nickel by bromine has been studied by x-ray diffraction techniques. The studies have revealed that the compound formed is $Ni_3O_4.\ 6H_2O$; it loses water of hydration at 70 and 160°C transforming to $Ni_3O_4.4.5H_2O$ and $Ni_3O_4.\ 3H_2O$ respectively and finally decomposes to a structure having particles of very small sub-division.

X-Ray Studies on Nickel Oxide Hydrates
Part 1—Hydrated Products

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Introduction

The structural characteristics of the different forms of oxides and oxide hydrates of nickel often cropped up during investigations of the crystalline phases in the corrosion products smeared out of the surfaces of the nickel-plated iron electrodes of the heavy water electrolysis plant at the Nangal unit of FCI Ltd. Moreover, the crystallochemical properties of different compounds of nickel have been an interesting object of study, especially with respect to their valency and water of crystallization. Thus, though nickel is divalent in its anhydrous oxide state, several workers in the past[1–14] have indicated the existence of its oxides and oxide hydrates having valency more than two. But in most of their studies the existence of higher valency of nickel do not seem to be confirmed though in certain cases some of these oxides and oxide hydrates had been identified and established by x-ray[4,12] and other techniques. Therefore, some attempts were made to prepare some of the compounds of nickel oxide hydrates independently and study them by x-ray diffraction techniques for their crystalline composition and structural properties.

Among the earlier workers who reported to have obtained the higher valency oxides and oxide hydrates were Belluci and Clavari[1,2]. They reported that the oxides prepared by wet methods were mixtures of hydroxide of nickel very unstable tetravalent nickel oxide hydrates of compositions $NiO_2\ XH_2O$ with no existence of Ni_2O_3.

Pellini and Meneghini[3] obtained a more stable peroxide of nickel by reacting hydrogen peroxide on nickel hydroxide or chloride in a caustic potash solution at very low temperatures. Howell[4] observed that sesquioxide and peroxide are simultaneously precipitated by the action of calcium and sodium hypochlorites on alkaline solution of nickel sulphate.

Francois and Delwaulle[5] studied the oxidation of nickel hydroxide by a basic solution of sodium persulphate and deducted that nickel hydroxide [Ni $(OH)_2$] is first oxidized to nickelic oxide (Ni_2O_3) and then to nickel dioxide (NiO_2). The mixture of Ni_2O_3 and NiO_2 remained in water up to 40°C, and then reduced to Ni_2O_4 which itself decomposed to Ni $(OH)_2$ at higher temperatures. Dede and Zieriacks[6] contradicted this and stated that the peroxide is not formed in the course of reaction and attributed the slight excess of oxygen ratio corresponding to sesquioxide to absorption of oxygen on the precipitated products by catalytic decomposition of persulphate. Besson[7,8] has put forward an evidence of Ni_3O_4 and Ni_2O_3 considered as alkaline oxides of NiO_2-2NiO and NiO_2NiO, obtained from oxidation of a nickel sulphate with persulphate, hypochlorite, bromite and iodite as well as hydrogen peroxide, oxygen and ozone.

Hutting and Peter[9] obtained (and confirmed by x-rays) $Ni_2O_3.H_2O$ by drying the precipitate given by the oxidation of divalent nickel solution by strong alkaline solution of hyprobromide at O°C. He also showed that the monohydrate could be obtained by heating the preparations by wet methods to 200°C in an autoclave by suspension in water and it decomposed to nickel monoxide water and oxygen under a pressure of 10 mm. of mercury at 138°C. Goralevich[10] prepared $H_2Ni_2O_4.nH_2O$, $H_4Ni_2O_5$ nH_2O, $H_4Ni_3O_6.nH_2O$ and $H_2Ni_3O_5.nH_2O$ by oxidation of nickel hydroxide by bromine or chlorine with caustic soda. He gave the structural formula $Ni(OH)_4$, where the nickel has a tendency to replace hydrogen and the first compound would be $(OH)_2Ni{<}^{O}_{O}{>}Ni$. Cairns and Ott[11] isolated an identified $Ni_2O_3.2H_2O$, $Ni_2O_3.H_2O$, $Ni_3O_4.2H_2O$ and $Ni_6O_7.3H_2O$ from the compounds obtained by oxidation of nickel nitrate solution containing alkaline hypobromide. Glemser and Enierhand[12] obtained α- NiOOH, and $Ni_3O_2(OH)_4$ by precipitation from potassium nickel cyanide with persulphate solution or nickel nitrate with hypobromide solution and have deduced their structure by x-ray diffraction measurements.

Some workers have separated the oxides of nickel by electrolytic deposition. Wernicke[13] obtained $Ni_2O_3.2H_2O$ by anodic precipitation of alkaline solution of nickel tartarate. Glemser and Enierhand[12] and Seiyama *et al*[14] obtained β - NiOOH, $Ni_3O_2(OH)_4$, $4Ni(OH)_2$—NiOOH and $Ni(OH)_2$ by electrolysis of alkaline nickel sulphate in sodium acetate solution and confirmed these by x-rays. Thus, though the existence of some of the hydrates have been established by x-rays, still the existence of other oxide hydrates and higher oxides have not been proved so far.

Experimental

For the preparation of nickel oxide hydrates, the previous workers had adopted either chemical or electrolytic processes. In some cases, both processes had yielded the same compound[4,12]. Therefore, to start with, the chemical methods of preparation have been followed. A divalent salt of nickel, viz. nickel nitrate, was treated with sodium hydroxide and was oxidized with bromine. These reactions yielded a light green-dark blackish precipitate, which was filtered and dried over sulphuric acid in cold.

In order to get an idea about the loss of water of hydration and crystalline phase transformations, linear plot of percentage weight-loss and a differential plot of weight-loss against rise in temperature were obtained for the dried greenish black precipitate. The differential plot showed three sharp peaks at 70, 160 and 330°C indicating certain phase transformations (Fig. 1A). Therefore, to obtain these transformation products the initial compound was heated separately at 80, 180 and 330°C in air. In each case, the heating temperature was maintained to about 3 hr.

These different samples were used to obtain x-ray powder diffraction photographs using a Guinier camera with bent quartz crystal reflected monochromatic CuKα radiation. The 'd' values were measured and the intensities of the lines were estimated visually.

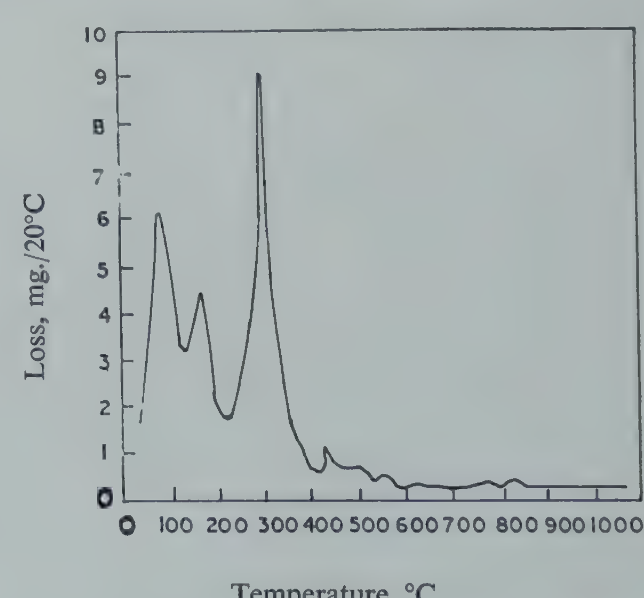

Fig. 1A—Differential Plot of Weight-Loss vs Temperature of Nickel Oxide Hydrate

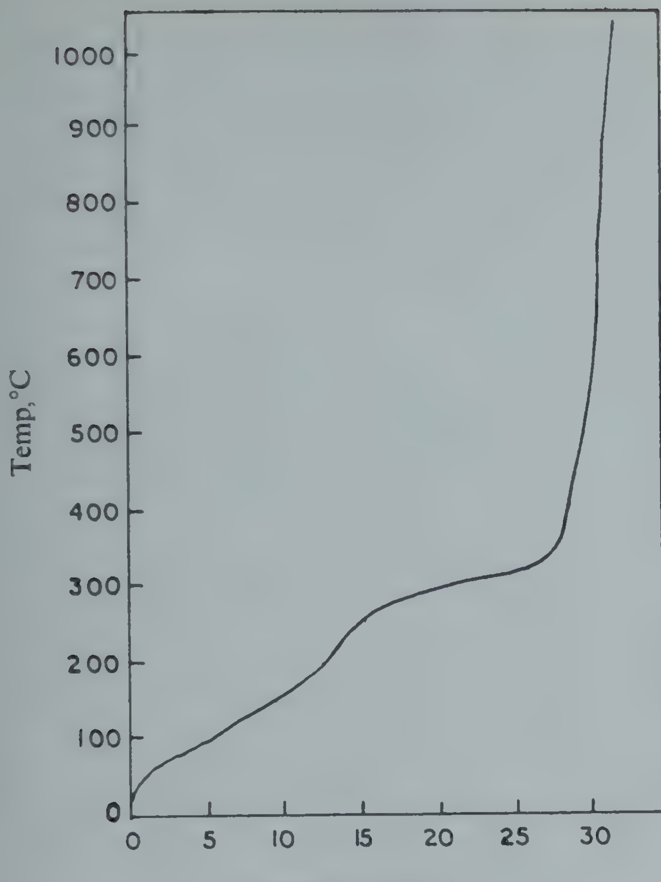

Fig. 1B—Linear Plot of Percentage Weight-Loss vs Temperature of Nickel Oxide Hydrate

Results and Discussion

There were marked differences in the x-ray diffraction patterns obtained from samples heated to various temperatures (Fig. 2 and Table 1). The patterns obtained from the original dried precipitate and the samples heated at 80 and 180°C showed certain crystalline phases. The sample heated at 330°C gave faint and diffuse bands at the positions corresponding to those of NiO phase indicating that the crystalline phases has decomposed to particles of very small dimensions having an NiO type structure.

For the identification of the crystalline phases in the prepared and subsequently heated samples, x-ray diffraction data of the compounds, viz. $Ni(OH)_2$, $4Ni(OH)_2$ NiOOH, $Ni_3O_2(OH)_4$, α—NiOOH, β—NiOOH and γ- NiOOH reported so far were consulted. But none of these agreed with the corresponding data of our samples. Obviously, the prepared samples were some form of nickel oxide hydrate for which no evidence or x-ray data is available. Therefore, attempts were made to assign certain empirical formula to the prepared nickel oxide hydrates by determination of molecular weights using x-ray method.

The determination of molecular weight consists of calculating the unit cell parameters from x-ray data and measuring the density. For the unit cell parameter determinations, the reciprocal lattice method was followed. The $\frac{1}{d^2_{hkl}}$ or Q_{hkl} values obtained for all powder lines and Qs for all observed Q_{hkl} values were calculated. The Q values which repeated several times were tried as reciprocal lattice parameters for systems of high symmetry. Values which gave satisfactory agreements between the observed and calculated Q_{hkl} values for all the lines were chosen as reciprocal unit cell parameters. From these, the direct cell parameters and hence volume of the unit cell were calculated, for each compound. Then, if M is the molecular weight of the substance,

$$M = \frac{V_o \text{ (in Å}^3) \times p_o}{1.672 \times 10^{-24} \times n}$$

where V_o is the volume of the unit cell, p_o the density in g./cm³ at N.T.P., 1.672×10^{-24} the mass of a proton in g. and n the number of molecules per unit cell. The density measurements were done by the displacement method and were corrected to N.T.P.

Prepared Sample: From the appearance of sharp lines in the diffraction pattern, the compound was assumed to be crystalline in nature. The analysis of diffraction data showed that it belongs to cubic system having the unit cell dimension a_o = 15.91Å. The average measured density was 2.45 g./cm³. As this was a compound of nickel oxide hydrate different forms were considered.

(i)
(ii)
(iii)
(iv)

Fig. 2—X-Ray Diffraction Photographs of Nickel Oxide Hydrates with Guinier Camera and Crystal Reflected in CuKα Radiation

(i) Original Sample Prepared & Dried (ii), (iii) and (iv) Sample Heated to 80, 180 and 330°C.

TABLE 1—X-RAY DATA OF NICKEL OXIDE HYDRATES

Sample at Room Temperature					Sample Heated to 80°C					Sample Heated to 180°C				
dÅ	I/I_1	Qobs	Qcal	hkl	dÅ	I/I_1	Qobs	Qcal	hkl	dÅ	I/I_1	Qobs	Qcal	hkl
11.33	s	0.0078	0.0079	110	11.33	vvw	0.0078	0.0079	002					
7.80	w	0.0164	0.0158	200	7.50	ms	0.0172	0.0178	003	7.14	s	0.0196	0.0198	003
6.50	vvw	0.0237	0.0237	211	5.60	vvw	0.0318	0.0316	004	3.55	w	0.0793	0.0792	006
										3.07	vvw	0.1061	0.1078	007
5.60	ms	0.0319	0.0316	220	4.50	vvw	0.0493	0.0494	005	2.71	vw	0.1362	0.1368	110
4.60	m	0.0473	0.0474	222	3.75	vw	0.0711	0.0711	006	2.67	m	0.1403	0.1408	008
4.25	vw	0.0554	0.0553	321	2.71	vw	0.1366	0.1369	100	2.50	m	0.1600	0.1566	113
3.85	vvw	0.0675	0.0672	410,322	2.67	m	0.1409	0.1389	101	2.335	vw	0.1834	0.1824	200
3.74	m	0.0715	0.0711	411,330	2.50	vvw	0.1605	0.1600	009	2.13	vvw	0.2204	0.2200	0,0,10
3.25	vvw	0.0947	0.0948	422	2.32	vw	0.1858	0.1863	105	1.76	vvw	0.3228	0.3232	208
2.975	vvw	0.1130	0.1146	520,432	1.56	vvw	0.4109	0.4107	110	1.56	w	0.4109	0.4104	300
2.70	vw	0.1372	0.1383	531	1.53	vw	0.4272	0.4285	113	1.54	vvw	0.4217	0.4192	302
2.65	m	0.1424	0.1423	600,442						1.51	vvw	0.4386	0.4312	0,0,14
2.58	w	0.1502	0.1501	611,532						1.48	vvw	0.4565	0.4568	1,1,10
2.395	m	0.1745	0.1738	622										
2.34	vw	0.1826	0.1817	631										
2.16	vw	0.2143	0.2133	721,633,552										
1.92	vw	0.2713	0.2726	821,742										
1.755	vw	0.3247	0.3240	910,833										
1.72	vvw	0.3380	0.3396	921,761,655										
1.56	vw	0.4109	0.4108	10,2,0; 862										
1.53	w	0.4272	0.4266	10,2,2; 666										
1.515	w	0.4357	0.4345	10,3,1; 952,765										
1.475	vw	0.4595	0.4582	10,4,0; 864										
1.42	vvw	0.4959	0.4977	11,2,1;10,5,1; 963										

s—strong, ms-medium strong, m-medium, w-weak, vw-very weak, vvw-very very weak.

Then, if the compound was assumed to be Ni_3O_4. $6H_2O$, the calculated density for this with sixteen molecules per unit cell would be 2.31 g./cm^3. As this value was very near to that of the observed value, the precipitate dried at room temperature was assumed to be the hydrate $Ni_3O_46H_2O$.

Assignment of this formula $Ni_3O_4.6H_2O$ for the oxide hydrate was supported also by the weight-loss experiments (Fig. 1b). The total weight-loss for the hydrate when it was completely dehydrated above 900°C was 31 per cent (Table 2). If the entire water of hydration were lost the percentage weight-loss for $Ni_3O_4.6H_2O$ would be 31. This excellent agreement corroborates the assumption that the compound is $Ni_3O_4.6H_2O$.

TABLE 2—PERCENTAGE WEIGHT-LOSS OF NICKEL OXIDE HYDRATE ON HEATING TO HIGHER TEMPERATURES

Sl.	Temperature, °C	Weight-loss, %	
		Experimental	Calculated
1.	70, (125)*	7.5	7.5
2.	160, (225)	14.8	15.5
3.	300, (400)	28.0	31.0
4.	900	31.0	31.0

*The values in brackets show the temperature of completion of transformation.

Sample Heated to 80°C: There is a change in the diffraction photograph of this substance from that of the previous one. Indexing of the x-ray lines and determination of unit cellparameters showed that this compound belongs to hexagonal-type lattice with a_o = 3.12 Å and c_o =22.50 Å. With the measured density of 2.86 and calculated unit cell parameters, the molecular weight came to be 324. This is very near to that of a monomolecular substance having the formula Ni_3O_4 $4.5H_2O$ (mol. wt. 321). If the weight-loss for the water of hydration was calculated for the transformation from $Ni_3O_4.6H_2O$ to Ni_3O_4 $4.5H_2O$, the value came to be 7.5 per cent. This was in good agreement with the experimental value of 7.5 per cent observed at 125°C (Table 2), where the differential plot showed the completion of the transformation. Therefore, it was deduced that Ni_3O_4. $6H_2O$ loses water of hydraton and transforms to a new structure at 70°C having the formula Ni_3O_4 $4.5H_2O$.

Sample Heated to 180°*C*: This substance also showed the diffraction pattern of a crystalline material, different from both the previous ones. Analysis of the powder diffraction data showed that this also belongs to a hexagonal system with the unit cell parameters a_o = 5.41 Å and c_o = 21.32 Å. The measured density was 3.62. Then the total molecular weight came to be 1184. If the compound is assumed to be $Ni_3O_4.3H_2O$, the total molecular weight for four molecules per unit cell is 1176 which is is almost the same as the experimental value. When the weight-loss was calculated for the transformation from Ni_3O_4. $6H_2O$ to Ni_3O_4. $3H_2O$, it came to be 15.5 per cent. This value was in good agreement with the observed value of weight loss of 14.8 per cent at 225°C where the differential plot showed the completion of this transformation. Therefore, it was concluded that the oxide hydrate loses further water of hydration and transforms to $Ni_3O_4.3H_2O$ at about 160°C.

Sample Heated to 330°*C*: The diffraction pattern of this sample did not indicate any crystalline material, but showed only broad and diffuse bands at the positions of the diffraction lines of NiO crystals. The differential weight-loss experimental showed a final large peak at 300°C and the experiment total loss in weight after completion of transformation at 400°C was about 28 per cent. On further heating, there was a very slow weight-loss which came to 31 per cent around 800°C. Beyond 900°C, no further weight-loss was indicated. This final value is the same if the entire water of hydration is lost from the hydrate $Ni_3O_4.6H_2O$. This means that the previous crystalline hydrate is completely disintegrated at 300°C giving up all its water of hydration and becoming completely anhydrite beyond 900°C.

A significant observation in the x-ray diffraction photographs of the hydrates was that the spacing shown by the hydrate at room temperature at 11.33, 5.60 and 3.74 Å were slowly disappearing along with the removal of water of hydration. These lines became very very weak for the hydrate heated to 80°C and totally disappeared for the hydrate heated to 180°C. Contrary to this, the 7.80Å line moved towards lower values and became more and more intense with the rise in heating temperature. These changes may be due to the removal of easily removable water molecules formed at certain interplanar distances as are indicated by the above spacings. The cubic cell of the hydrate at room temperature transformed to hexagonal systems after transformations at 70 and 170°C. These indicate that the water of hydration forms a definite part in the structure and loss of water of hydration in part or full brings about transformations to new structures. Thus, the crystallographic transformations and finally its complete decomposition to a NiO type structure of particles of very small sub-division at 300°C prove that the water molecules are not simply chemically adsorbed but have gone into formation of definite hydrate structures.

Conclusion

Thus, the x-ray studies on the nickel oxide hydrate precipitated by oxidation of alkaline divalent nickel by bromine showed that it is an oxide hydrate of the type Ni_3O_4 $6H_2O$, in which nickel may be in a higher valency state than two. This hydrate transforms gradually to lower hydrates on heating in air, the transformations occurring at 60°C and 170°C to $4.5H_2O$ and $3H_2O$ states respectively. The transformations are restricted only upto a stage of $3H_2O$ and on further heating it completely decomposes instead of transforming to lower oxide hydrates.

Acknowledgement

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Further studies on the nickel oxide hydrates showed that with the rise in heating temperature the disintegrated structure of the dehydrated hydrate at 300°C passes through the intermediate structure formations of Ni_2O_4 and Ni_3O_4, which are slightly modified defect structures of nickel oxide (NiO). It has also been found that with the rise in heating temperature the crystalline particle size of these defect structures increases with the removal of defect structures and replacement of crystalline structure of nickel oxide. At 1000°C the dehydrated products take up completely a crystalline structure of nickel oxide.

X-Ray Studies on Nickel Oxide Hydrates Part 2—Dehydrated Products

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Introduction

In an earlier paper[1] it has been shown that the oxidation of an alkaline divalent nickel solution by bromine yielded a precipitate of nickel oxide hydrate of the type $Ni_3O_4.6H_2O$ which on heating to higher temperature in air transformed to oxide hydrates of lesser number of molecules of water of hydration. Thus, it was shown that $Ni_3O_4.6H_2O$ transformed to $Ni_2O_4.4.5H_2O$ at 60°C and

to $Ni_3O_4.3H_2O$ at 170°C, and the entire structure disintegrated at 300°C to a non-crystalline structure of particles of very small sub-division showing only diffuse and broad bands in the x-ray diffraction photograph. Therefore, further studies on the hydrate heated to higher temperatures have been made in order to understand the formation as well as the growth of the crystalline structure for the dehydrated products.

Experimental

The original precipitate was divided into several portions and were heated separately at 330, 450, 550, 650, 750, 850 and 1000°C in air for about 3 hr. Each sample was used in a Debye-Scherrer camera of 11.46 cm. diam. with filtered radiation as well as in a Guinier camera in conjunction with crystal reflected beam of Cu Kα radiation to obtain powder diffraction photographs. The photographs were subsequently used to obtain microphotometric traces to estimate the integrated intensities of the diffractions lines. Crystalline particle size determination by measurement of line breadth at half peak intensity[2] was also done for all the heated products. The Guinier photographs were made use of to observe any variation in 'd' values from sample to sample.

In some cases density determination by displacement method with carbon tetrachloride solution was also made.

Results and Discussion

The diffraction photographs of the hydrate heated at 330°C did not show a regular crystalline pattern, but diffuse and broad bands at the positions of the NiO structure. The other samples which were heated at higher temperatures did not also show any change in the crystallographic pattern from the one heated at 330°C, but only showed a progressive sharpening of the diffraction lines with the increase in temperature (Fig. 1). It was also observed that there were appreciable variations in intensity for the lines from sample to sample as well as from NiO. Therefore, the observed relative integrated intensity values of all powder lines of all samples were corrected for Lorentz-polarization and multiplicity factors and the values were scaled with respect to 200 reflection taken as hundred to compare with the cal-

Fig. 1—X-ray Diffraction Photographs of Dehydrated Products of Nickel Oxide Hydrate with Powder Cameras of 11.46 cm. Diam. and Filtered CuKα Radiation

(a to g: samples heated to 330, 450, 550, 650, 750, 850 and 1000°C respectively)

TABLE 1—X-RAY DATA OF DEHYDRATED PRODUCTS

	Observed Intensities of Dehydrated Products at, °C							Calculated Intensities of				
hkl	330	450	550	650	750	850	1000	4 NiO	Ni_3O_4	Ni_2O_4	mod. Ni_3O_4	mod. Ni_2O_4
111	14	22	27	32	38	33	38	39	26	11	31	13
200	100	100	100	100	100	100	100	100	100	100	100	100
220	92	85	80	81	80	75	71	68	68	66	87	87
311	14	21	22	28	30	30	28	25	19	10	20	11
222	29	39	40	49	54	60	53	51	49	48	51	44
400*				52	57	44	39	41	40	37	55	50
331				17	19	20	22	19	14	8	17	8
420				24	30	28	33	33	32	28	34	26
422				26	32	30	28	27	25	23	36	31
511, 333				8	12	14	14	17	13	11	17	11

*The observed intensity values of the dehydrated products at 330°, 450° and 550°C for the reflections 400 and higher indices could not be estimated due to high back-ground blackening in the photographs.

culated intensity values of the NiO structure. The absorption and temperature factor do not introduce much error and therefore these have not been considered to correct the observed values.

A comparative study (Table 1) shows that the intensity of powder lines with h, k and l (all odd) are smaller and those with h, k and l (all even) are larger than the corresponding calculated intensity values of NiO structure[3]. These differences are more pronounced for the samples heated at lower temperatures (330 and 450°C) and are slowly reduced by the rise in heating temperatures. This indicates the possibility of formaton of structural particles of Ni_3O_4 and Ni_2O_4 as intermediate products, during dehydration to nickel oxide while heating. These intermediate products would have the same structure as that of NiO with a difference that half or a quarter of the nickel atomic sites in the lattice may be vacant since the intensity of the reflections with h, k and l all odd are reduced because of the structure factor.

$F_{hkl} = 4f_{Ni} - 4f_o$ for such reflections. But, though, an actual calculation of the intensities of reflections and scaling of the values with respect to 200 reflection as hundred for structures Ni_3O_4 and Ni_2O_4 did show some appreciable changes in intensities of reflections with h, k, l all odd towards the observed intensity values, these structures could not explain the observed increase in intensities of reflections with h, k, l all even. Therefore a modification to the structures of Ni_3O_4 and Ni_2O_4 were thought of in the following lines.

If there is a NiO defect structure formation in the form of Ni_3O_4 or Ni_2O_4 there may be Ni atomic site vacancies in the unit cells either at cube corners or at face centres or both. Whenever there are vacancies at the corner and adjacent face centres during the disintegration of the hydrate structure and formation of the NiO structure, a Ni atom may take the tetrahedral positions in the cubic cell forming a tetrahedral co-ordination with the oxygen atoms at the body centre and nearest side centres. When intensities of reflections of such a trial structure of Ni_3O_4 and Ni_2O_4 were calculated, their values moved towards those of the observed ones. But they were too high to agree with the observed ones. Therefore intensities for another trial structure of the same type with tetrahedrally co-ordianted Ni atoms occupying only one in four unit cells were calculated and this time the agreement was fair between the calculated and observed intensity values. Thus the observed intensity data of dehydrated products at 330 and 450°C were agreeable with those of the calculated ones of modified Ni_2O_4 structure and the observed intensity data of the dehydrated products at 550°C and above were agreeable with those of modified Ni_3O_4 structure.

The reasonable agreement between the experimental densities of dehydrated products at 330, 550 and 850°C and calculated densities (Table 2) also show the possibility of formation of such intermediate structures. In both these modified structures of Ni_3O_4 and Ni_2O_4, the nickel atoms are bivalent in octahedral co-ordinations like a regular NiO structure while the tetrahedrally co-ordinated extra nickel atoms—about one in four unit cells—may be in tetravalent linkage so as to adjust the electrical neutrality of the substance. In such an arrangement the electrical neutrality may not be complete and hence the structure may be metastable. The crystalline particles composed of these structures may also be very

TABLE 2—CRYSTALLINE PARTICLE SIZE AND DENSITY VALUES OF THE DEHYDRATED PRODUCTS

No.	Dehydrated Products at, °C	Particle Size, Å	Observed Density, g./cm³	Calculated Density, g./cm³
1.	330	41	3.8	4.2 (Ni_2O_4)
2.	450	48	—	—
3.	550	53	4.0	—
4.	650	112	—	—
5.	750	223	—	—
6.	850	380	5.6	5.5 (Ni_3O_4)
7.	1000	>1000	7.0	6.9 (4 NiO)

small. In fact, a crystalline particle size determination from powder diffraction lines showed that the crystalline particle size of the dehydrated product at 330°C is very small, around 40 Å in dimensions. Up to 550°C the particle size grows only to around 50Å, still retaining the defect structures. These structural particles when heated at higher temperatures slowly shift the Ni atoms from tetrahedral to octahedral co-ordinations, growing simultaneously more and more in regular crystalline structure and in crystalline particle size dimensions. Thus at 850°C, the particle size grows to around 400 Å and at 1000°C to more than 1000Å in dimensions taking up a stable and regular crystalline structure of NiO.

The evidence of tetravalent nickel atoms of the dehydrated products at lower heating ranges of the present study indicates the possibility of existence of tetrahedral co-ordination for nickel in the hydrate structures pre-prepared at room temperature and in the subsequent transformation products. Probably because of this, the hydrate structures, after collapse of their definite crystalline structure above 300°C did not take up immediately the regular crystalline structure of NiO. The slightly lower value in percentage weight-loss (28 per cent instead of 31) after completion of transformation of $Ni_3O_4.3H_2O$ at about 400°C shows that though the hydrate structure has disintegrated it has not completely given up its excess oxygen atoms of water molecules or otherwise or the water molecules as such of which a part or in full might have been in the tetravalent co-ordination in the hydrate structures. The rather very slow rate of loss in weight during heating from 400 to 900°C till the total loss equated to the loss of entire water of hydration may be due to the giving up of excess oxygen atoms or water molecules existing in tetrahedral co-ordinations and slow transformation of these to more stable bivalent co-ordinations of NiO structures.

Conclusion

The x-ray studies of the dehydrated products of nickel oxide hydrate of the type $Ni_3O_4.6H_2O$ reveal that above 300°C it collapses to a defect NiO type structure without any water of crystallisation. This defect structure passes through the structural forms of Ni_2O_4 and Ni_3O_4 having crystalline particles of very low dimensions in which tetrahedrally co-ordinated nickel atoms are found to exist in approximately one in four unit cells of the defect structures. By rise in heating temperatures the tetrahedral co-ordinations are replaced by octahedral co-ordinations and the defect structures are slowly removed and ultimately at 1000°C the dehydrated products take the regular crystalline structure of NiO.

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The Cretaceous sedimentary rocks of the Tiruchirapalli and Pondichery areas contain glauconites of diversified origin. An attempt has been made to evaluate the genesis of this characteristic mineral and its relation to sedimentation during that period.

A Study of Glauconites from Cretaceous Limestones Of Tiruchirapalli and Pondichery

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Introduction

The Cretaceous rocks in Tiruchirapalli and Pondichery areas occupy discontinuous patches surrounded by the Archaean and older metamorphics. A good amount of stratigraphic as well as palaeontological work has been done on these marine rocks by various workers. In a recent seminar[1] on the Cretaceous Tertiary Boundary of this area, the new findings on the basis of stratigraphy as well as palaeontology were discussed.

The glauconites are very widely studied and they are quite important for the age determination of sediments by the estimation of potassium/argon ratio. In India, the mineralogy of the glauconites was studied in a detailed manner in case of the Vindhyan rocks by Srivastava.[2] However, studies have not been made in respect of the glauconites of the Cretaceous rocks, except for a cursory mention of its presence by the previous workers.[3] In the present paper a detailed mineralogical study of the glauconites from this area is reported for the first time. The author[4] was able to note the wide occurrence of this mineral during a detailed study of the phosphatic nodules of Tiruchirapalli area. Glauconites are found to be associated with all the important phosphorites of the world and as such the presence of glauconite can be used in arenaceous carbonate occurrence as an indicator for the possibility of phosphorite occurrence. This can be applied in the case of Indian orthoquartzite-carbonate sequence of different ages wherever glauconites also occur.

Another important utility of glauconite is that it may be used as a raw material for potash. In India, huge deposits of the glauconites have been found in the Vindhyan rocks, which can be studied from this point of view since this country does not have any rich potash deposits.

Petrology of the Glauconites

The samples were collected mainly from the Ariyalur and Pondichery areas. The phosphatic nodules of the Uttatur stage of the Ariyalur area and also the limestones of the horizons E and F of Pondichery are the important rocks containing the mineral.

The mineral was studied in thin section as it was not possible to isolate it separately due to its intimate association with carbonates. The glauconites occur as detrital pellets as well as the replacement of some microfossils. A few grains are agglomerated to form nodules and are cemented by brown phosphatic materials which give yellow coloration on spot test by vanadium molybdate. The glauconite grains are rounded, elliptical as well as having the form and appearance of microfossils which they replace. On the basis of colour, the pellets can be classified as grass green and pale green types and an intermediate between them. The grass green and the pale green types are uniform in colour with those tints and show a higher birefrinigence. The variegated pellets show a colour mottling under low magnification.

Grass Green Pellets: These pellets show a fine scaly appearance (Fig. 1); under crossed nicols, they show uniform mottling in colour. The pellets are penetrated by radially disposed surface shrinkage (syneresis) cracks that are wider at the margin and are becoming narrow and converging towards the centre. These cracks are filled with opaque brown material. The walls of the

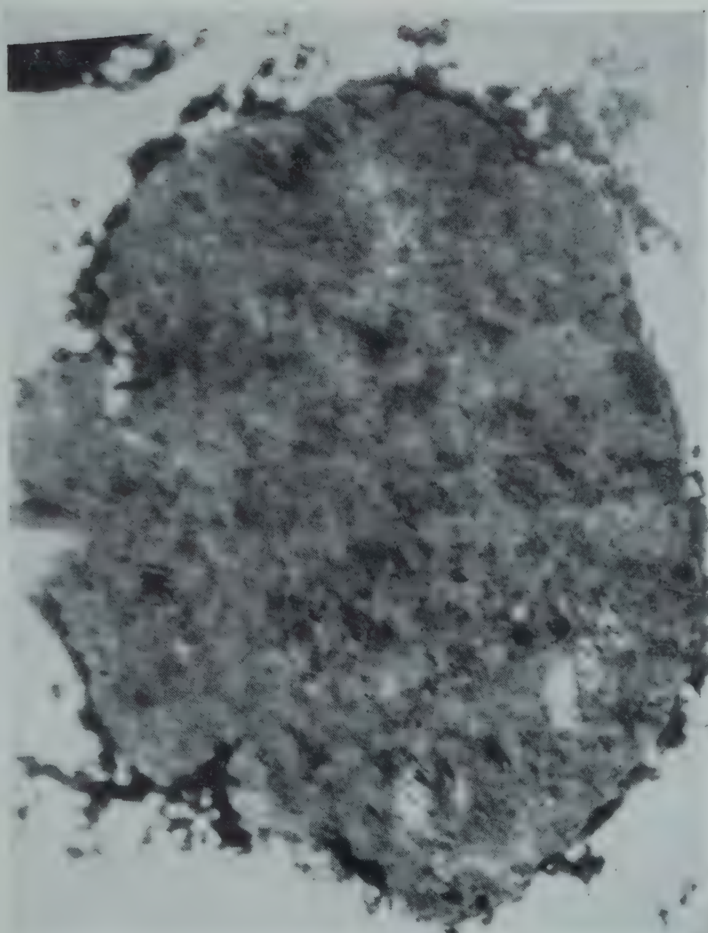

Fig. 1—Grass Green Pellet Showing Scaly Appearance ($\times 100$)

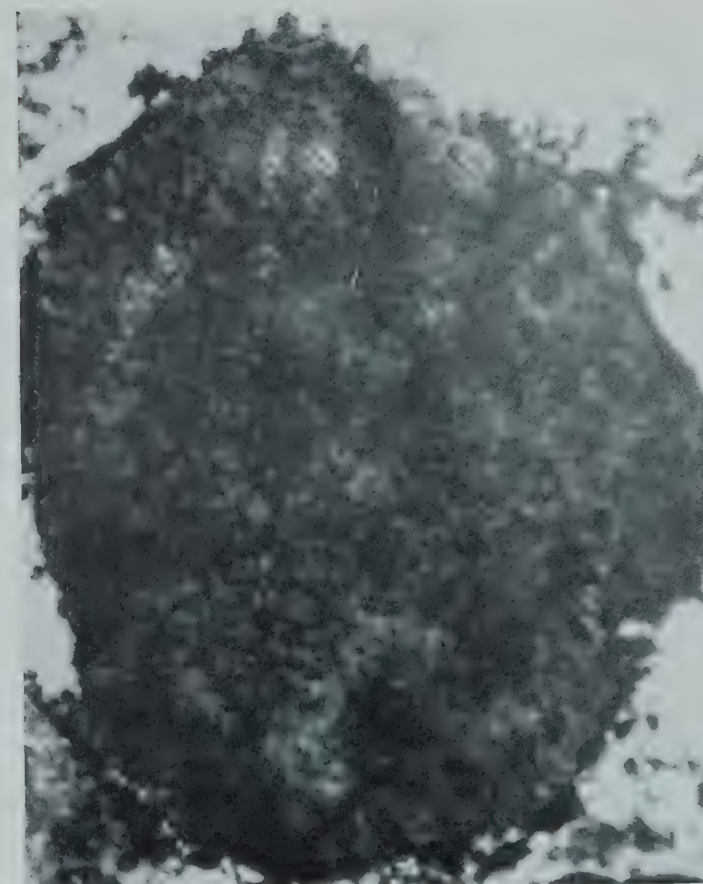

Fig. 3—Variegated Pellet Showing Interwoven Crystallites ($\times 100$)

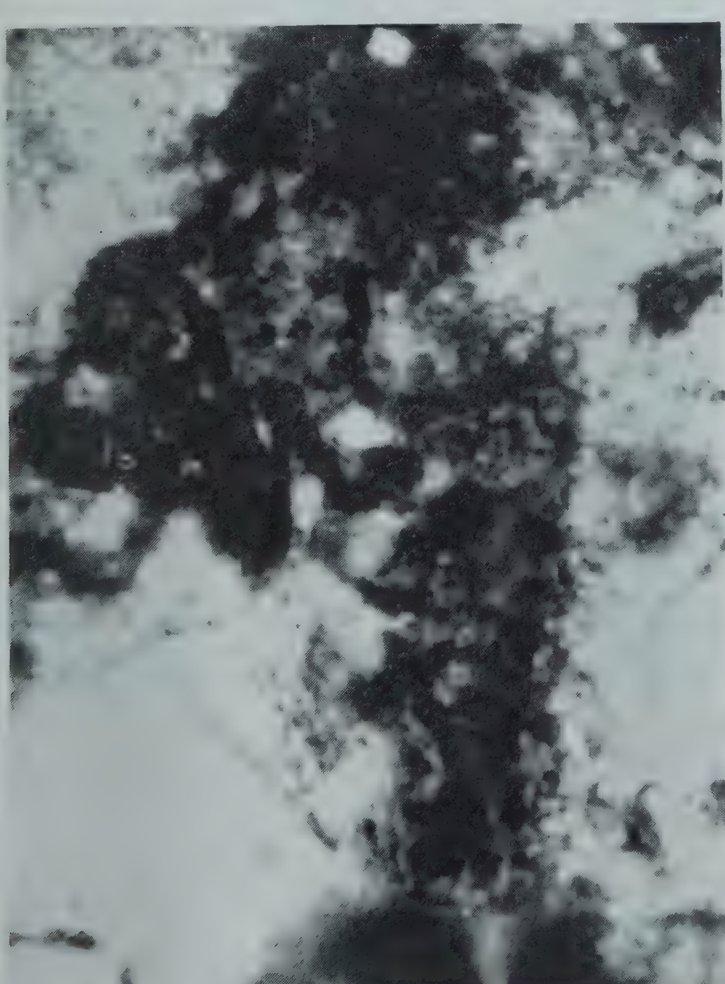

Fig. 2—Pale Green Pellets with Rounded outline ($\times 100$)

Fig. 4—A Biserial Test of Foraminifera Showing the Replacement by Glauconite ($\times 25$)

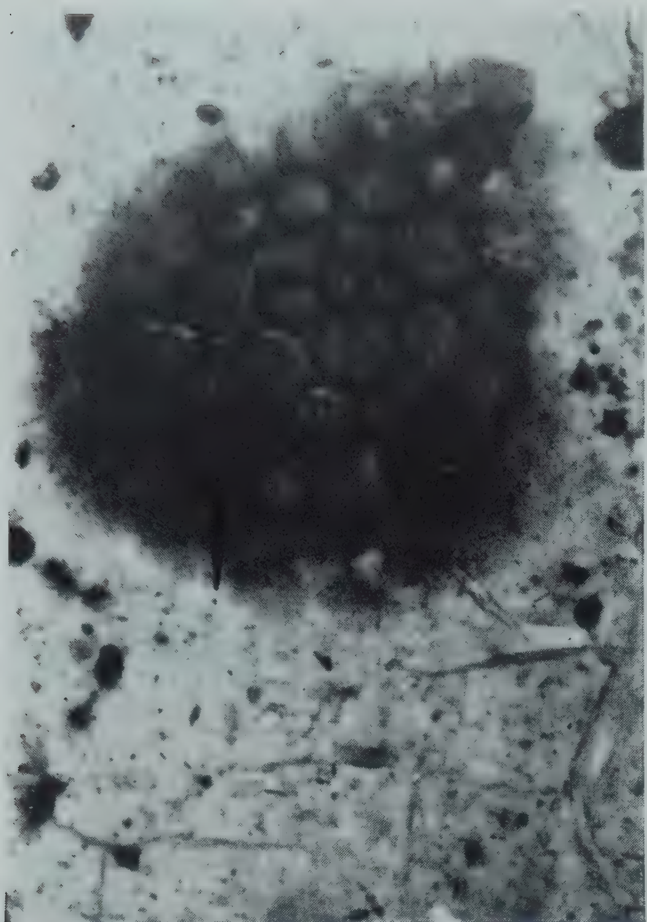

Fig. 5—A Honeycomb Structure Test Replaced by Gluconite (×100)

Fig. 6—Glauconite Forming as Cementing Material Around Detrital Grains (×100)

cracks are either straight or convex. Because of the cracking the pellet outline is prominently lobed. It may be assumed that semicircular and irregularly shaped pellets may be the dispersed products of disintegration due to cracking of the bigger pellets. The grass green pellets are detrital in nature and they are found mainly in the silty biomicrites of the Pondichery area.

Some of the grass green pellets appear to be made up of an amorphous dull brown coating around them due to oxidation. In some cases, the oxidation is complete resulting in the formation of a dull brown outer rim with a yellowish internal core. In the case of phosphatic nodules, the colours of the pellets vary, ranging from grass green to dark brown through the intermediate stage of yellowish brown.

Pale Green Pellets: These pellets occur abundantly in phosphatic nodules. They are generally pale yellowish green and show a nonlobate structure. Under crossed nicols, they show micro-aggregate texture. The surface shrinkage cracks are absent and the absence of internal cracks is significant (Fig. 2).

The pale green pellets have a low birefrinigence showing circular to elliptical outlines. Many pale green and dark brown pellets are of the same size and shape. They must have been phosphatized to certain extent by the formation of collophane. In some cases, the grass green pellets have a pale green core and dark brown rim with gradual transition from yellowish green to dark brown.

Variegated Pellets: The variegated pellets occur in lesser quantity as compared to the above two and are bigger in size and show randomly interwoven crystallites resulting in the formation of curious clotted structure (Fig. 3). The grass green part shows a coarse crystalline habit having prismatic grass green flakes.

Replacement of Microfossils: The glauconite is observed as replacement of the various microfossils. In the fossiliferous limestone of Pondichery, the glauconite is observed as replacement of foraminefera. A typical example, where the uniserial globular test is replaced by the glauconite while the outer margin is brown in colour which may be due to oxidation, is shown (Fig. 4). In certain cases, partial replacement takes place resulting in the presence of glauconite patches in the microfossils (Fig. 5). The replacement is such that the original structure of the microfossil is retained.

Glauconite as Cementing Materials: In a few thin sections, glauconite occurs as a cementing material slowly corroding the detrital quartz grains. In the bivalve fragments (Fig. 6), it is observed that the thick ferruginous walls are dark brown in colour, which may be due to collophane, a phosphatic mineral. Inside the walls, the trapped detrital angular grains of quartz are observed to form a horizontal layer. The grains are held together by the micrite (recrystallized cement). This cement is replaced by the glauconitic material which is of grass green colour. The material has a regular granular form with a scaly appearance. The microcrystalline glauconitic material has replaced the detrital quartz grains along the margins.

Discussion

The conditions in which the glauconites have formed will indicate the nature of environment in which the sediments were deposited. The conditions for the formation of authigenic phosphates and glauconites are apparently same as indicated by the presence of both together. The two minerals appear to have formed preferably on the current swept banks and shoals where sediment accumulation is minimum and dissolved phosphatic and iron enrichment of local nature may be attained due to upwelling from adjacent deeps.[6,7]

The pellets appear as detrital grains in silty biomicrites with a lot of poorly sorted detrital grains of quartz and acid plagioclase and microfossils, cemented together by an impure microcrystalline calcite pointing to a cool and quiet environment. So it clearly points that the glauconite pellets have been transported from different sources along with the detrital material and have been mixed by the burrowing activity of micro organisms.

The pellets are of organic origin as the size and shape of the brown pellets are similar to the glauconite pellets. Partial glauconitization of brown pellets is also observed. The brown pellets in the initial stage are mainly composed of clay carbonate mixtures which later undergo phosphatization or glauconitization. According to Teodorovich (*see* Bailey and Atherin[8]) the pellets must have formed due to primary accretionary aggregates of colloidal particles which aged and crystallized in the sea bed. A detailed review on the colloidal particle accretion hypothesis has been made by Bailey and Atherton.[8]

In the recent years, a good amount of work has been done on the genesis of glauconite. According to Fairbridge[9], the glauconitization is favoured by cooler waters. He[9] suggested, on the basis of the distribution and mineralogy, that the glauconite is derived from clays, micas and felspars by slow hydration and ion-exchange process which is favoured by the slight reducing conditions together with a free access of sea water at a pH around 8. Reducing conditions can be established

in the open shelf in microenvironment, such as decaying interior of bivalve shell or of foraminifera or associated with fecal-pellets. According to Ojakangas and Keller[10] organic precipitation in a microenvironment seems to be the rule providing the correct Fe^{3+}/Fe^{2+} ratio. The glauconites are the product of halrmyrolysis according to Muller.[11]

The glauconites of the Cretaceous carbonate rocks of Tiruchirapalli and Pondichery areas have formed duet to organic processes.

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A mathematical analysis of the liquid hydrocarbon reforming process has been carried out and a set of empirical correlations have been obtained to determine the equilibrium composition of the reformed gas without involving any trial and error procedure. The values predicted from these results tally excellently with the data obtained by the conventional procedure as well as the procedures developed by Lihou and Dent.

Reformation of Liquid Hydrocarbons—A Mathematical Analysis

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Simplified empirical correlations have been obtained to determine the equilibrium composition of the reformed gas from liquid hydrocarbons. Equilibrium is reached spontaneously in the catalytic reforming of liquid and gaseous hydrocarbons. The design of reformers (gradient heaters) are, therefore, entirely based on thermodynamic principles. The conventional procedure for calculating the equilibrium composition of simultaneous reactions are extremely painstaking. Graphical[1], nomographic[2] and empirical[3] methods are also available but they do not cover the entire range a designer would need. In this paper, a set of expressions has been developed from the laws of graphics which enables to calculate the compositions over the wide ranges of temperature, pressure and steam to carbon ratios in the feed.

The catalytic reformation of liquid hydrocarbons consists of complex reactions, but using a highly selective catalyst and a proper grade of the feedstock reformation is carried out with steam to evolve hydrogen, carbon dioxide and carbon monoxide, with a little unreacted hydrocarbon in the form of methane. The gaseous hydrocarbons consist predominantly of methane (saturated gas), which is an intermediate product of the reaction at the initial stages of reforming[4] Liquid

hydrocarbons. Besides the saturated, some unsaturated gaseous hydrocarbons are also produced by the catalytic cracking of liquid hydrocarbons[4,5], the latter being most reactive and unstable under the conditions of reformation, undergo immediately reformation to account for the carbon dioxide and carbon monoxide present even at the earliest stages of reaction.

$$\left.\begin{array}{ll} C_nH_{2n} + nH_2O = nCO + 2nH_2 & \ldots\ A \\ Co + H_2O = CO_2 + H_2 & \ldots\ B \end{array}\right\} \quad ..(1)$$

Methane being the stablest hydrocarbon of the lot is reformed in the last stages according to methane-steam reaction.

$$\left.\begin{array}{ll} CH_4 + H_2O = CO + 3H_2 & \ldots\ A \\ CO + H_2O = CO_2 + H_2 & \ldots\ B \end{array}\right\} \quad ..(2)$$

As stated above, the liquid hydrocarbons are split up into lower gaseous hydrocarbons at the initial stages in the reformer. Dent[4] assumes an irreversible reaction in which the naphtha is converted into methane and carbon dioxide, according to the following stoichiometeric expression:

$$C_nH_{2n+2} + (n\text{-}1)/2.\ H_2O \rightarrow (3n+1)/4.\ CH_4 + (n\text{-}1)/4.\ CO_2 \quad ..(3)$$

In spite of the complex mechanism of the reforming reaction, its approach to equilibrium is so close that thermodynamic principles can be applied directly to determine the composition of the reformed gases at any operating conditions[1,4,5,6], studies with pure heptane have shown that in about 0.10 sec. residence time 90 per cent of the liquid hydrocarbons are reformed and within 0.15 sec. all the liquid hydrocarbons are reformed[5]. Thus for a given reformer and with a specified feedstock, the composition of the reformed gas is controlled by the operating variables, viz. temperature, steamcarbon ratio and pressure. The design of the reformer is based on the heat transfer criteria within the furnace, tube and the catalyst bed. As the composition of the gases changes enormously from the feed end to the exit, the heat transfer co-efficient also changes both along and across the axis of the tubes. In order to compute exact heat transfer co-efficient, compositions at various selected points down the reformer tube are required[1,6]. The methane leakage in the reformer can be taken as key component in establishing mathemetical analysis of the process and subsequently determining the efficiency thereof.

The percentages of methane, carbon dioxide, carbon monoxide and hydrogen in the reformed gas are functions of operating parameters, viz. (1) exit reformer temperature, (2) operating pressure (exit) (3) and moles of steam supplied per atom of carbon in the feed. Thus,

$$X = f(T, P \,\&\, F) \quad (4)$$

where X = methane in the reformed gas, %
f = Symbol function of
P = Absolute operating pressure, atm.,
T = Exit reformer temperature, °C., and
F = Ratio of moles of steam supplied in the feed to the atoms of carbon in the distillate.

The percentage of methane in the reformed gas increases with pressure and decreases with temperature and steam-carbon ratio (Fig. 1). Hence, it can be stated that per-

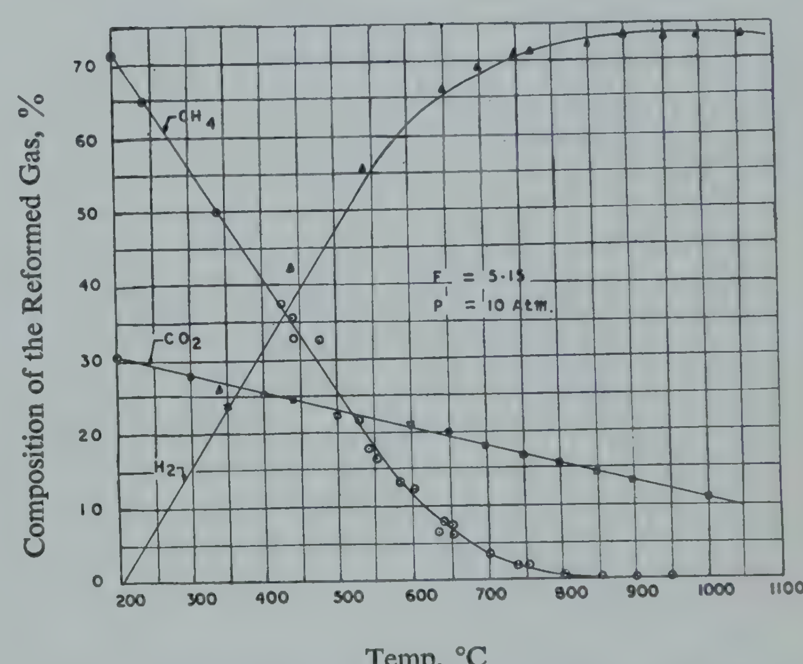

Fig. 1—Composition of the Reformed Gas vs Outlet Reforming Temperature at Constant Pressure (P) and Steam/Carbon Ratio (F)

centage of methane is a direct function of operating pressure and inverse functions of temepratures and steam-carbon ratio, or:

$$X = f'(P) \quad (5)$$
$$X = f''(1/T) \quad (6)$$
$$X = f'''(1/F) \quad (7)$$
$$X = f_1(P/TF) \quad (8)$$

or similarly,

$$Y = f_2(TF/P) \quad (9)$$
and
$$Z = f_3(F/T) \quad (10)$$

where Y and Z are the percentages of hydrogen and carbon dioxide in the reformed gas. The equilibria of shift conversion is not a function of perssure[4]. Again let,

$X = f'i\,(T)$ at constant pressure P and steam-carbon ratio F be denoted as

$$X = fi\,(T)\,PF \qquad (11)$$

and likewise

$$X = f_1''\,(P)\,TF \qquad (12) \text{ at constant T and F}$$
$$X = f_1'''\,(F)\,PT \qquad (13) \text{ at constant P and T}$$

In the expressions 11 and 12 if f_1' and f_1'' are similar functions, a linear relationship is obtained between T and P on eliminating X.

$$T = f^{\circ}\,(P)\,PF \qquad (14)$$

which denotes the effect of change of pressure at constant pressure and steam-carbon ratio F for which the expression 11 is valid. The effect of pressure is, therefore, reflected on the variable T, instead of change in percentage of methane. In other words, as regards the percentage of methane, the effect of increasing pressure is same as decreasing exit reformer temperature. Similarly, in the expressions 11 and 13, if f_1' and f_1''' are similar functions, the relation

$$T = f^{\circ\circ}\,(F)\,F\ \&\ P \qquad (15)$$

is obtained at constant F and P denoting the effect of F(i.e. steam-carbon ratio) on the percentage of methane in terms of equivalent change in reforming temperature.

If the functions f_1', f_1'' and f_1''' are not similar, no linear relationship is obtained. Instead, functions other than linear are obtained. However, by the application of the law of graphics these functions can be converted into linear functions with close approximations[8,9]. The problem then simplifies to solving simultaneous equations.

Rigorous conventional[6,10] as well as graphical calculations were done to determine the equilibrium composition of the reformed gas keeping the percentages of the components of the reformed gases as function of (i) exit reforming temperature at constant pressure and steam carbon ratio of 10 and 5.18 respectively, (ii) exit reformer pressure at constant temperature and steam carbon ratio of 850°C and 5.18 respectively and (iii) as moles of steam per atom of carbon in the feed to the reformer at constant temperature and pressure of 850°C and 10 atmospheres respectively. These are shown in Figs. 1 to 3. It can be observed from Fig. 1, that at the earlier stages, where the heavier hydrocarbons are split into lighter saturated as well as unsaturated gaseous hydrocarbons and the reformation of the unsaturates takes place predominantly clearly follows a linear relationship with respect to exit reforming temperature. This linearity in relationship exists till the exit reformer temperature approaches 550-600°C. The percentages of methane and carbon dioxide in the reformed gas decline linearly, methane with much greater gradient than cabnon dioxide. The rapid decline in percentage composition of methane is found to be

$$CH_4 = (101.75 - .15T)PF \qquad (16)$$

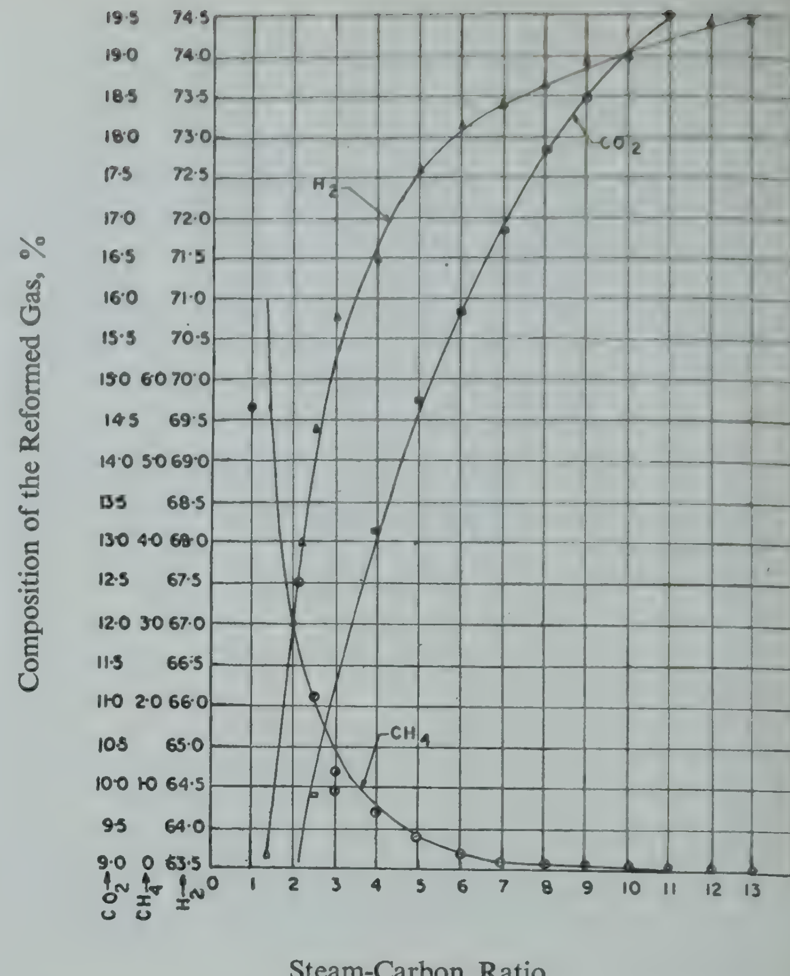

Fig. 2—Composition of Reformed Gas Against Steam-Carbon Ratio in the Feed at 850°C and 10 Atm.

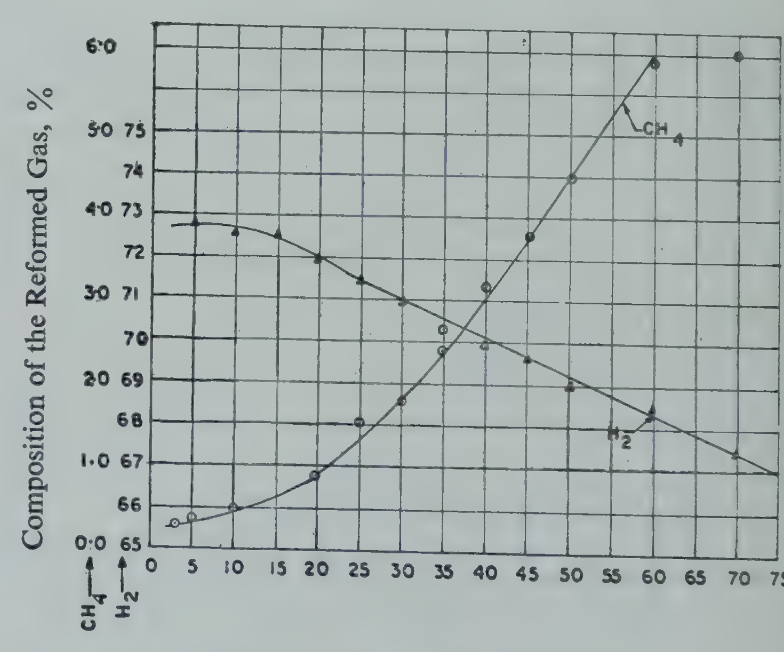

Fig. 3—Composition of Reformed Gas Against Exit Pressure at 850°C and F 5.18

This is valid upto 600°C, whereas the percentage of carbon dioxide continues to drop over the entire range of reformation but with a much less gradient than the methane gas,

$$CO_2=(35.5-2.4 \times 10^{-2}T) \quad PF \qquad (17)$$

This expression is true upto 1000°C of the reforming temperature. But on the other hand, percentage of hydrogen increases linearly with respect to the exit reforming temperature with about the same gradient as that of the methane up to 600°,

$$H_2= (-33.3 + .162T) \; PF \qquad (18)$$

At the higher temperatures of reformation, a zone where the catalyst encounters saturated hydrocarbons the process of reformation is retarded considerably and takes up an exponential path with reference to exit reforming temperature. Thus, the percentages of methane and hydrogen can no longer be predicted by expressions 16 and 18, instead they follow an exponential relationship as expressed,

$$Log_{10}\, CH_4 = 4.54 - 5.7 \times 10^{-3}\, T) \; PF \qquad (19)$$

$$Log_{10}\, H_2 = 1.666 + 2.4 \times 10^{-4}\, T) \; PF \qquad (20)$$

The equations 19 and 20 are true for all the temperatures between 550 to 1000°C and 600 to 900°C respectively.

The effect of steam-carbon ratio F(Fig. 2) on the reformation is same as that of temperature. With the increase of ratio F, the percentage of methane decreases and that of hydrogen increases exponentially. On the contrary, carbon dioxide increases the nature of which is not linear. As referred earlier, in this paper a linear relationship is obtained between temperature T and steam-carbon ratio F from expressions 16 and 13 giving,

$$T_{CH_4} = (610.0 + 47.5\, F)\; F \;\&\; P \qquad (21)$$

where T_{CH_4} is the equivalent change in temperature due to change in steam carbon ratio F. As the law of expression 13 is not known the expressions 13 and 16 cannot be solved to obtain expression 21. Instead, a graphical procedure is adopted which is very much simpler. A graph (Fig. 4) is constructed for equal values of methane for the corrosponding values of temperature from Fig. 1 as ordinate and steam-carbon ratio from Fig. 2 as abscissa. The determination of the constants for the straight line so obtained gives the expression 21. Similarly, from the same figures we obtain following relation for hydrogen (Fig 6).

$$T_{H_2} = (567.5 + 55.9F) \; PF \qquad (22)$$

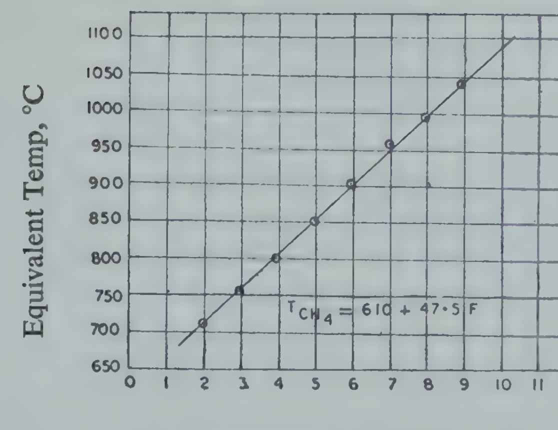

Fig. 4—Effect of Steam-Carbon Ratio (F) on Equivalent Change in Temperature

A relationship between equivalent change in temperature for carbon dioxide against steam-carbon ratio can be obtained by solving the expression 17 and 23 which has been obtained after converting the non-linear relationship of Fig. 2 (Scale 3) which is plotted in Fig 5.

$$CO_2 = 4.83 + 14.6 \log_{10}F \qquad (23)$$

and from expressions 17 and 23,

$$T_{CO_2} = 1245 - 580.0 \log_{10}F \qquad (24)$$

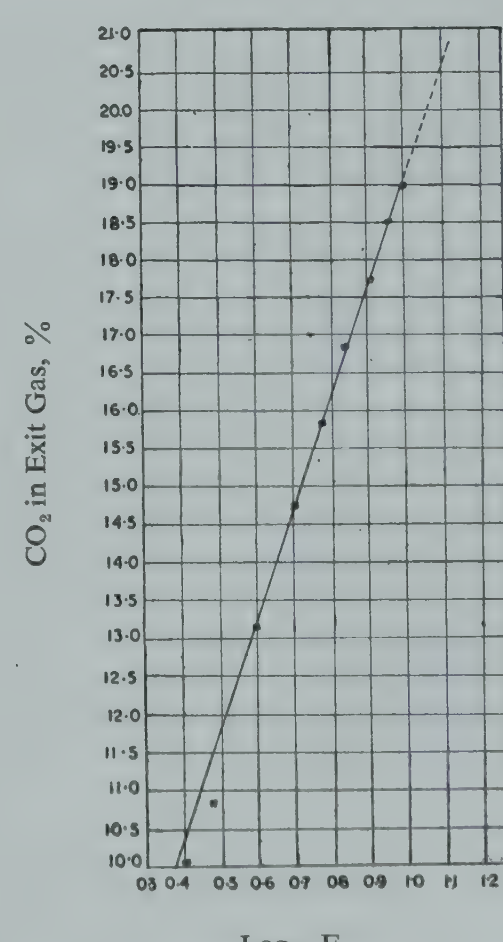

Fig. 5—Carbon Dioxide vs Steam-Carbon Ratio at 850°C and 10 Atm.

which agrees excellently with the Fig. 6, drawn on the procedures explained earlier.

The effect of increasing the exit reformer pressure is to inhibit the reforming reactions. With the increase of pressure the precentage of methane in the reformed gas also increases at first slowly from 5 to 15 atm, then rapidly. On the other hand, the percentage of hydrogen, as expected, reduces uniformly with a considerable gradient.

The shift conversion reaction within the reformer is practically not affected by the exit pressure.[4] A straight line parallel to abscissa is obtained (not shown in Fig. 2). Since the effect of increasing pressure is to retard reforming reaction, the nature of the curves in Fig. 3 is just the reverse of that of Fig. 1. In Fig. 1, the decrease in percentage of methane is rapid at the initial stages of reformation, thereafter it retards and finally the curve of methane against reforming temperature becomes asymptotic. The initial part of the Fig. 3 is similar to the final portion of the curve in Fig. 1, and the zone in between are alike. Since the expression 11 has already been determined earlier it is convenient and accurate to establish relationship between T and P graphically. The relationship so obtained, viz.

$$T_{CH_4} = (1043.0 - 193.0 \log_{10}P) \qquad (25)$$

is lograthmic. The above plot is a curvilinear and plotted in Fig. 7. The effect of increasing pressure on the percentage of hydrogen in the reformed gas is such that it gradually reduces with a uniform gradient. But hydrogen as a function of temperature has three modes of

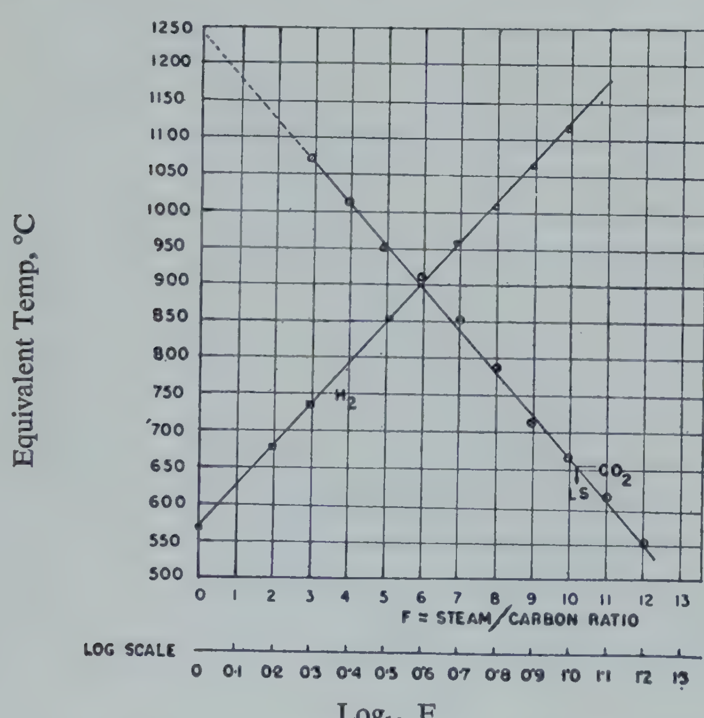

Fig. 6—Effect of Steam-Carbon Ratio on Equivalent Change in Temperature

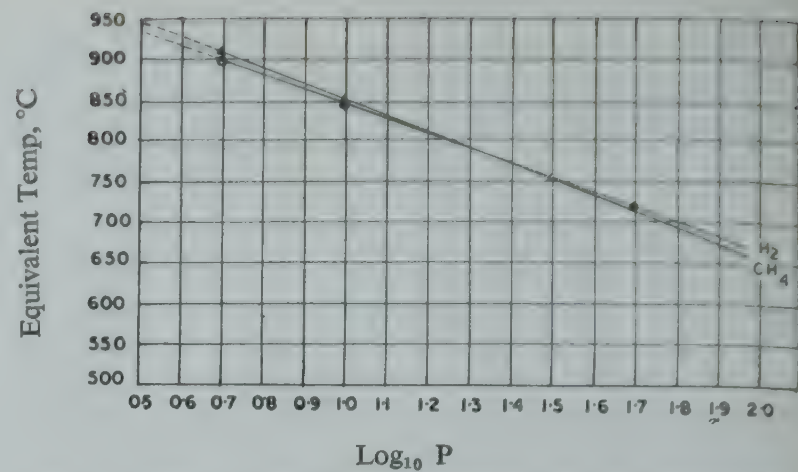

Fig. 7—Effect of Exit Reformer Pressure on the Equivalent Change in Temperature at Constant Pressure of 10 Atm. and Constant Temperature 850°C

relationship. At first it is linear, than exponential and and finally asymptotic. It is, therefore, very much obvious that the related functions are not at all similar. This is also obtained in a similar fashion and found to be:

$$T_{H_2} = 1028.5 - 178.5 \log_{10}P \qquad (26)$$

Calculation Procedures

The calculations of the composition of the reformed gas at various operating parameters are done most conveniently by the use of Figs. 1 to 7. However, the calculations give accurate results. In Fig. 1 the percentages of the constituents of the reformed gas have been plotted as a function of the exit reformer temperature whereas in Figs. 2 and 3 the temperature has been kept constant at 850°C. Consequently, this particular value of the reformation temperature becomes a reference point, and any departure in temperature (T_D) from this reference point due to changes in pressure P and steam-carbon ratio F, therefore can be referred to as 'Rise or Drop' in temperature. Thus, for a given condition if the value of T_D obtained from any one of the equations 21, 22, 24, 25 and 26 is in excess or less than the reference point, they are Rise and Drop in temperature respectively. They also indicate that the effect of the changes are either to increase or decrease the reforming temperature at the conditions of Fig. 1.

T_{DF} = Rise or drop in temperature due to steam carbon ratio,

T_{DP} = Rise or drop in temperature due to pressure,

T_O = Overall rise or Drop in temperature, and

T_E = The effective reforming temperature,

then $T_O = (T_{DF} \pm T_{DP}) \qquad (28)$

and $T_E = (T \sim T_O) \qquad (29)$

The value of T_E so obtained is substituted in one of the relevant exptessions viz. 16, 17, 18, 19 and 20 and the percentage of the desired constituent is calculated. The following example will illustrate the procedure of calculations.

Illustration 1

A reformer producing gas for the synthesis of methanol is being run at the following conditions: (a) pressure 15 atm, (b) steamcarbon ratio 4 and (c) exit reforming temperature 865°C. It is required to calculate the equilibrium composition of the gas.

Methane:

(1) The effect of pressure is given by the expression 25.
$T_{CH_4} = 1043.0 - 193.0 \log_{10}P = 816°C$.
$T_{DP} = 850\text{-}816 = -34°C$.
Alternatively, the value of $T_{CH_4} = 816°C$ can be directly read from Fig. 7.

(2) The effect of steam-carbon ratio F is given by the expression 21.
$T_{CH} = 610.0 + 47.5\ F = 800°C$
Alternatively, $T_{CH_4} = 800°C$ can be read directly in Fig. 4 for methane.
: $T_{DP} = 850 - 800 = 50°C$
and
$T_O = -(50 + 34) = -84°C$
$T_E = (865\text{-}84) = 781°C$
Substituting the value in expression 19,
$\text{Log}_{10}\ CH_4 = 4.54 - 5.7 \times 10^{-3}\ T_E = +0.09$:
$CH_4 = 1.021$ per cent
Alternatively, $CH_4 = 1.021$ per cent can be read directly from Fig. 1.

Hydrogen:

(1) The effect of pressure on hydrogen is given by 26 (Fig. 7).
$T_{H_2} = 1028.5 - 178.5 \log_{10}P = 818.5°C$
Alternatively from graph $T_{H_2} = 818.5°C$
$T_{DP} = (850 - 818.0) = -31.5°C$

(2) The effect of steam-carbon ratio is shown by expression 22
$T_{H_2} = 567.5 + 55.9F = 791°C$
Alternatively from Fig. 6, $T_{H_2} = 790°C$
$T_{DF} = (850 - 791.0) = -59.0°C$
$T_O = (31.5 + 59.0) = -90.5°C$
Hence $T_E = (865 - 90.50) = 774.5°C$
Substituting the values in expression 20,
$\log_{10} H_2 = 1.666 + 2.4 \times 10^{-4} \times T = 1.8523$:
$H_2 = 71.2$ per cent.
Alternatively H2 = 71.5 per cent from Fig. 1 against 774.5°C

Corbon Dioxide:

(1) Effect of pressure = Nil

(2) Effect of steam carbon ratio F is shown by expression 24,
$T_{CO_2} = 1245 - 580.0 \log_{10}F = 895°C$
$\therefore T_{DF} = (895 - 850) = +45.0°C$
$T_E = 910°$; substituting the values in 17.
$CO_2 = 35.5 - 2.4 \times 10^{-2}\ 910 = 13.7$ per cent
Alternatively $CO_2 = 13.7$ per cent against 910°C in Fig. 1.

Hence, the composition (in percentage) of the re-reformed gas is $H_2 = 71.2$, $CO_2 = 13.7$, $CO = 14.08$ and $CH_4 = 1.021$.

Illustration 2

A reformer for the synthesis of ammonia is operating at 30 atm. 810°C exit reformer temperature and steam carbon ratio 3.4. It is required to calculate the equilibrium composition of the reformed gas.

Methane:

(1) The effect of pressure,
$T_{CH_4} = 1043 - 193.0 \log_{10}P = 758.0°C$;
$T_{DP} = -92.0°C$

(2) The effect of steam-carbon ratio F,
$T_{CH_4} = 610 + 47.5F = 771.4$; $\therefore T_{DF} = -78.6°C$
Hence $T_O = -(78.6 + 92.0) = -170.6°C$
And $T_E = (810 - 170.6) = 639.4°C$
Finally $\log_{10}CH_4 = 4.54 - 5.7 \times 10^{-3} \times 639.4 = 0.92$
$\therefore CH_4 = 7.75$ per cent

Hydrogen:

(1) The effect of pressure,
$T_{H_2} = 1028.5 - 178.5 \log_{10}P = 765°C$
: $T_{DP} = -(850\text{-}765) = -85.0°C$

(2) The effect of steam-carbon ratio,
$T_{H_2} = 567.5 + 55.9F = 757.5$, $T_{DF} = (850\text{-}757.5) = -92.5$
$\therefore T_O = -177.5°C$
and $T_E = (810 - 177.5) = 632.5°C$
$\therefore \log_{10}H_2 = 1.666 + 2.4 \times 10^{-2} \times 632.5 = 1.818$
$H_2 = 65.85$ per cent

Carbon Dioxide:

The effect of steam-carbon ratio,
$T_{CO_2} = 1245 - 580.0 \log_{10}F$

$= 936.44°C$; $\therefore T_{DF} = (936.44 - 850) = 86.44$

$T_E = 810 + 86.44 = 896.44$

$CO_2 = 35.5 - 2.4 \times 10^{-2} \times 896.44 = 14.0$ per cent

The composition of the reformed gas is, $H_2 = 65.85$ per cent, $CO_2 = 14.0$ per cent, $CO = 12.4$ per cent and $CH_4 = 7.75$. The value of CH_4 so obtained agrees excellently with the values given by "Andrews". The results obtained by this procedure agrees well with those of various authors.

Acknowledgement

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EDITOR'S NOTE

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With a view to study the relative efficiencies of nitrogenous and phosphatic fertilizer combinations including carbonitric form of nitrophosphate (16:13 grade) with and without potash application, experiments were carried out over a two years' period on *Pusa Sawani* variety of *bhindi*. This study revealed that response to nitrophosphate, ammonium sulphate plus superphosphate and urea plus superphosphate averaged over levels of potash was significant over control but not significant between themselves. The response to potash averaged over all treatment combinations of nitrogen and phosphate was found to be non-significant. Even though in cases of nitrophosphate, ammonium sulphate plus superphosphate and urea plus superphosphate the addition of potash showed increasing trend in yield, it was found statistically non-significant.

The response to nitrogen and phosphate as ammonium sulphate and superphosphate was non-significant while that to urea was found significant when averaged over potash levels. As a single nutrient application, urea gave significantly higher yield either over ammonium sulphate, superphosphate or combinations of nitrogen and phosphate.

Efficacy of Nitrogenous and Phosphatic Fertilizers on Growth and Yield of *Bhindi: (Abelmoschus esculentus L)*

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Bhindi is an important and popular warm season vegetable cultivated under varied soils and agroclimatic conditions of tropical and sub-tropical parts of this country. It is grown for its tender, immature fruits which are very rich in mineral elements, like iron, calcium, magnesium etc. Although it is widely cultivated throughout India, practically no information is available about the optimum fertilizer need and response of this common vegetable to different fertilizers.[1]

The Agronomical Wing of this Division of FCI Ltd., besides working out the crop response to different fertilizers, is engaged with field testing of different new fertilizer products, including different grades of nitrophosphates, for a future project pattern, since their manufacture is not going to involve import of sulphur. Extensive trials are being carried out on varying soils and climatic conditions using different grades of nitrophosphates and the results indicate that on equivalent nitrogen and P_2O_5 basis, both sulphonitric (50 per cent water and 50 per cent citrate-soluble P_2O_5) and carbonitric (wholly citrate-soluble P_2O_5) forms of nitrophosphate are almost at par with other nitrogenous and phosphatic fertilizer combinations on paddy, wheat, potato, etc.[2,3]. In a series of experimentations employing various combinations and grades of nitrophosphates and other fertilizers, the present investigation was undertaken on *bhindi* to test the response in yield to some nitrogenous and phosphatic fertilizer combinations including carbonitric form of nitric phosphate with and without potassium.

Materials and Method

The experiment was conducted during the rainy seasons of 1968 and 1969 at Sindri. The soil analysis data of the experimental plot are presented in Table 1.

TABLE 1—Chemical Soil Analysis (Oven-dry basis)

Organic carbon, %	0.308
Available N, %	0.030
Available P_2O_5, kg/ha	10.2
Available K_2O, kg/ha	450
pH	7.8
Conductivity	0.21

The experiment consisted of a randomized block design of 14 treatments replicated three times. The levels of nitrogen, P_2O_5 and K_2O were 60, 30 and 30 kg/ha respectively, arbitrarily fixed from some general recommended publication. The plots were in the form of beds 5.4×4.0 meters and rows were 60 cm. apart and plants

TABLE 2—DETAILS OF FERTILIZER APPLICATIONS IN THE EXPERIMENT

No.	Abbreviation	Treatment	Requirement of Different Fertilizers for the Plot Size 21.6 sq.m.		
1.	NP + K	Nitrophosphate + Muriate of Potash	249.65 g. AS	498.51 g. NP	108.22 g. KCl
2.	AS + SP + K	Ammonium Sulphate + Superphosphate + Muriate of Potash	648.00 g. AS	405.00 g. SP	108.22 g. KCl
3.	U + SP + K	Urea + Superphosphate + Muriate of Potash	281.23 g. U	405.00 g. SP	108.22g. KCl
4.	NP	Nitrophosphate	249.65 g. AS	498.51 g, NP	—
5.	AS + SP	Ammonium Sulphate + Superphosphate	648.00 g. AS	405.00 g. SP	—
6.	U + SP	Urea + Superphosphate	281.23 g. U	405.00 g. SP	—
7.	SP + K	Superphosphate + Muriate of Potash	—	405.00 g. SP	108.22 g. KCl
8.	AS + K	Ammonium Sulphate + Muriate of Potash	648.00 g. AS	— —	108.22 g. KCl
9.	U + K	Urea + Muriate of Potash	281.23 g. U	— —	108.22 g. KCl
10.	AS	Ammonium Sulphate	648.00 g. AS	—	—
11.	U	Urea	281.23 g. U	—	—
12.	SP	Superphosphate	—	405.00 g. U	—
13.	K	Muriate of Potash	—	—	108.22 g.
14.	C	Control (No manure)	—	—	—

50 cm. apart within the row. 3 to 4 seeds were sown in each hole, and about 10-12 days after germination the resulting seedlings were thinned out to one. The variety used was *Pusa Sawani*.

Nitrogen was applied either as ammonium sulphate or urea and nitrophosphate, phosphorus as single superphosphate and nitrophosphate and potassium as muriate of potash. The fertilizers were weighed and half of nitrogen, i.e. 30 kg. and the whole of P and potassium applied as basal dose in rows and mixed thoroughly with the soil in laid out beds before sowing. The rest of nitrogen was applied after one month of sowing also in rows between the plants. The amounts of fertilizer applied under different treatments are given in Table 2.

The sowing was done on the 15th and 17th June 1968 and 1969 respectively. The growth data in terms of plant height and the number of leaves per plant were recorded after a month of sowing at fortnightly intervals. Harvesting started by the end of July when the fruits were 14-16 cm long and tender as vegetable. Thereafter, harvesting was done in alternate days and continued upto the last week of September. Yield from each plot was weighed in the field at each harvest and the total yield for the three replicates of each treatment was averaged for statistical analysis.

Results and Discussion

(a) *Growth*: The data on plant height and number of leaves treatment-wise were averaged both for replications and years (Table 3). The data presented consist of last record after 75 days of sowing.

TABLE 3—AVERAGE HEIGHT AND LEAF NUMBER IN *Bhindi*

Treatment	Height, cm.	No. of Leaves/plant
NP + K	92.0	27.4
AS + SP + K	81.7	26.8
U + SP + K	88.4	28.7
NP	85.7	26.1
AS + SP	78.0	22.4
U + SP	75.2	23.7
SP + K	69.7	21.6
AS + K	80.7	24.7
U + K	85.1	22.8
AS	76.6	23.4
U	75.7	23.2
SP	67.2	21.1
K	69.5	22.3
C	63.5	19.4

It reveals from the Table 3 that NPK combinations (i.e. all the three nutrients) registered maximum growth in terms of height as well as number of leaves. But among nutrients in double combinations, i.e. NP, PK or NK, NK was most effective in inducing growth followed by those of NP and PK. In single nutrient combinations, nitrogen was most effective as either ammonium sulphate or urea and they showed identical growths as to height and leaf number whereas phosphorus and potassium showed very much reduced growth almost parallel to no manure treatment. From periodical observations it was noticed that wherever ammonium sulphate or urea was applied maximum growth was attained in early stages whereas nitrophosphate showed it in later stages and finally levelled up or surpassed the other ones in about 2 months period. Nevertheless, when the growth data were statistically analysed to correlate with yield no significant differences were observed.

(b) *Yield*: The yield data were pooled for both the years and presented in Table 4.

The statistical analysis of fruit yield data indicates clearly significant differences due to the different fertilizer treatments. The response to nitrogen and phosphate as ammonium sulphate and superphosphate was found to be nonsignificant while that to urea was significant over control when averaged over potash levels. Nitrophosphate, ammonium sulphate plus superphosphate and urea plus superphosphate averaged over levels of potash were found to be significant over control and also over ammonium sulphate and superphosphate, but not over urea treatment, which was found non-significant. Urea resulted a higher yield over all the other fertilizers, viz. ammonium sulphate, superphosphate, muriate of potash and nitrophosphate.

While comparing the three nitrogen and phosphate treatment combinations, i.e. nitrophosphates, ammonium sulphate plus superphosphate and urea plus superphosphate, they were found non-significant. The average response to nitrophosphate over control was 35.42 qn/ha and that to ammonium sulphate plus superphosphate 30.89 qn/ha and to urea plus superphosphate 34.46 qn/ha. These results clearly indicate that in case of *bhindi*, which is about 130-140 days crop, even carbonitric form of nitric phosphate when compared with common nitrogenous and phosphatic fertilizer combinations on equal nitrogen P_2O_5 basis, is by no means inferior under normal conditions. This finding corroborates the results obtained in potato and field crops carried out by this Wing[2–4] and those of others.[5]

The response to potash averaged over all treatment combinations of nitrogen and phosphate was found to be non-significant. This is because since the soil is rich in available potash content (Table 1), added potassic fertilizer did not give significant increase in yield.

Ammonium sulphate when applied alone gave significantly higher response over no manure plot but when applied in combination with potash yield was found depressed. This was also true in case of urea. But in cases of superphosphate or no manure plot, this depressing trend was not there as evidenced from Table 4. In cases of nitrophosphate, ammonium sulphate plus superphosphate and urea plus superphosphate, the addition of potash generally showed increasing trend in yield, though found statistically non-significant. Ahmad *et al*[6] obtained best yields of *bhindi* at 122 kg/ha N, 168 kg/ha P, and 280 kg/ha K levels of application on River Estate loam soils of Trinidad. The response at these higher levels may be due to the poor nature of Trinidad soil, whereas the positive response to nitrogen, phosphorus and negative response to potassium in the present experiment is clearly accountable to soil composition of Sindri.

The economics of manuring for treatment combinations containing nitrogen and P_2O_5 in presence and absence of K_2O only are presented in Table 5. The cost of fertilizer has been taken at the existing levels and the

TABLE 4—Yield of *Bhindi*, qn/ha

Treatment	O	SP	AS	U	NP	AS + SP	U + SP	Mean
O	40.49	52.25	71.86	76.86	76.07	78.76	78.37	67.81
K	59.31	57.41	57.72	63.68	94.49	82.81	90.28	72.25
Mean	49.86	54.79	64.79	70.27	85.28	80.75	84.32	70.03

C.D. at 5% level for treatment means: 25.81
C.D. at 5% level for K treatment means: 9.47
C.D. at 5% level for marginal treatment means: 18.50

TABLE 5—ECONOMICS OF FERTILIZATION ON *Bhindi*

Treatment	Yield, te.	Price of Produce, Rs.	Cost of Manuring, Rs.	Nett Profit Over Control, Rs.	Nett Profit on per Rupee Investment, Rs.
Control	4.04	2424	—	—	—
NP	7.61	4566	269.97	1872.03	6.93
AS + SP	7.88	4728	218.63	2085.37	9.54
U + SP	7.84	4704	179.41	2100.69	11.71
NP + K	9.45	5670	295.92	2950.08	9.97
AS + SP + K	8.28	5268	244.58	2599.42	10.63
U + SP + K	9.03	5418	205.36	2788.64	13.58

value of the produce at Rs. 600/te which was the then the market value of *bhindi*.

From Table 5 it is evident that nitrogen and phosphorus application on *bhindi* gave highest profit per rupee invested in the form of U + SP, giving a ratio of 1: 11.71. With AS and SP it worked out to 1: 9.54 and the lowest was with NP, i.e. 1: 6.93. The above combination in presence of potassium showed similar trend, viz. highest with U + SP + K (1: 13.58), with AS + SP + K 1: 10.63 and with NP + K 1: 9.97. It was, however, clear that potassium was most effective in presence of NP than U and AS in presence of SP and K to produce a profit on a rupee investment basis.

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The addition of the ten calcium salts, viz. calcium chloride, calcium iodide, calcium bromide, calcium acetate, calcium nitrate, mono-calcium phosphate, calcium oxide, calcium carbonate, calcium-sulphate and calcium silicate, under three different water treatments A, B and C has been found to increase the availability of nitrogen and phosphorus in two slightly acidic (Sarnath) and highly acidic (Ranchi) soils. Generally, under high initial soil moisture (treatment B) and alternate wetting and drying conditions (treatment C) maximum availability of nitrogen and phosphorus with the addition of 8 to 16 m.e./100 g. soil of calcium carbonate and calcium acetate respectively was obtained.

Changes in the Measure of Available Nitrogen and Phosphorus in Acid Soils in Presence of Calcium Salts

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The addition of calcium salts to both acid and alkali soils induces a number of beneficial effects thus bringing about a condition in them suitable for plant growth and development[1]. Salts like calcium sulphate improve the alkali soils and calcium carbonate is known to ameliorate soil acidity. Thus, calcium salts appear to be very much useful under extreme conditions of soil pH of both alkali and acid ranges. Quite recently, Ali[2], while studying the effects of a few calcium salts on the availability of nitrogen and phosphorus in a few acid soils, observed that addition of calcium salts increases the availability of soil nitrogen and phosphorus. Much work on the effect of other calcium salts on the availability of nitrogen and phosphorus with other soils under different pH levels, however, still remains undone. In this paper, an attempt has, therefore, been made to study the effect of ten calcium salts, viz. calcium chloride, calcium iodide, calcium bromide, calcium nitrate, calcium acetate, mono-calcium phosphate, calcium oxide, calcium carbonate, calcium sulphate and calcium silicate, on the availability of nitrogen and phosphorus in two acid soils (Ranchi and Sarnath).

Experimental

Two acidic soils were collected from the surface (0″-6″) from Ranchi (Bihar) and Sarnath (Varanasi), U.P. The samples were then pulverized in an agate mortar and passed through 100 mesh (BSS) sieve. The soils were then chemically analysed by the reported methods[3] (Table 1).

TABLE 1—Physico-Chemical Composition of Soils

Constituents	Ranchi (Bihar) Soil, %	Sarnath (Varanasi) Soil, %
HCl-insoluble	74.45	72.25
Total Fe_2O_3	7.53	5.40
Total Al_2O_3	12.00	12.25
Total CaO	0.09	0.72
Total MgO	0.54	0.85
Total N	0.03	0.07
Total P_2O_5	0.09	0.13
Total C	0.30	0.56
C/N ratio	10.00	8.00
Available N	0.0052	0.0150
Available P_2O_5	0.0200	0.0700
Total C.E.C.	17.84 m.e./100 g.	19.52 m.e./100 g.
Exchangeable H^+	10.00 „ „	3.50 „ „
Exchangeable Ca^{2+}	10.31 „ „	12.50 „ „
Exchangeable Mg^{2+}	5.91 „ „	6.35 „ „
pH	5.10	6.40
Texture	Clay loam	Loam

For observing the effect of calcium salts on the availability of nitrogen and phosphorus in both the soils, the following three treatments were given:

Treatment A: In treatment A, 100 g. of the soil sample was taken in a 150 ml. pyrex beaker and 20 ml. of distilled water was added in the beginning either as such or in the form of calcium salt solution and distilled water keeping the total valume of liquid added the same. After 15 days, the same amount of water was added again.

Treatment B: In this case, 40 ml. of distilled water or partially in the form of calcium salt solution and remaining distilled water as mentioned in treatment A was added to 100 g. of soil. After 15 days of incubation at 30°C (with$\pm$ 2°C), 20 ml. of distilled water was added again.

Treatment C: This treatment consists of alternate wetting and drying, i.e. before the addition of calcium salts, 30 ml. of water was added to 100 g. soil and was then allowed to dry in an oven at about 105°C, cooled and then treated again with the same amount of water and dried as above. Then 20 ml. water was added (as in treatment A) at the start of the experiment and thereafter 15 days of incubation.

In all the three treatments, the calcium salts equivalent to 1, 2, 4, 8, 16 and 20 m.e./100 g. soil were added.

After the period, the soils were pulverized in an agate mortar and analysed for available nitrogen and also for phosphorus colorimetrically[5,6].

The pH values were measured[7] by a Leeds and Northrup pH meter. The intitial pH values of the treated soils after the addition of calcium salts were determined before these were kept in glass chamber for 30 days' incubation.

For each set, a control (having all the treatments except calcium salts addition) was run side by side.

Results and Discussion

The data (Tables 2 and 3) show clearly the effect of ten calcium salts on the availability of nitrogen and phosphorus in a highly (Ranchi) as well as a slightly (Sarnath) acidic soils under the three treatments A, B and C. The two tables (Tables 2 and 3) also show the effect of different calcium salts with 8 m.e./100 g. soil, known to be the optimum concentration for all the calcium salts under the above treatments in both the acidic soils. However, the only exception is calcium carbonate which gives the maximum availability of nitrogen and phosphorus in the highly acidic (Ranchi) soil at 16 m.e./100 g. soil. It has been generally observed that the treatment B (initially good supply of moisture) gives the maximum availability of nitrogen in both the acidic soils, whereas the maximum availability of phosphorus pentoxide has been found to be in the following order of treatments: C> B> A.

The order of efficiency of the calcium salts in relation to the availability of nitrogen and phosphorus under all the treatments in highly acidic (Ranchi) soil has been found to lie in the following order:

Available Nitrogen

$CaCO_3 > Ca(H_2PO_4)_2 > CaSO_4 > CaO > CaCl_2 > Ca(CH_3COO)_2 > CaI_2 > CaSiO_3 > CaBr_2$

Available P_2O_5

$CaCO_3 > CaO > CaI_2 > CaSO_4 > Ca(CH_3COO)_2 > Ca(NO_3)_2 > CaCl_2 > CaBr_2 > CaSiO_3$

In the case of slightly acidic (Sarnath) soil with the same treatments, viz., A, B and C, the effect of the calcium salts on the availability of soil introgen and phosphorus has been found to be in the following order:

Available Nitrogen

$Ca(CH_3COO)_2 > CaO > CaI_2 > Ca(H_2PO_4)_2 > CaCO_3 > CaSO_4 > CaCl_2 > CaBr_2 > CaSiO_3$

Available P_2O_5

$Ca(CH_3COO)_2 > Ca(NO_3)_2 > CaO > CaSO_4 > CaCO_3 > CaCl_2 > CaI_2 > CaBr_2 > CaSiO_3$

From the above orders, it is evident that the application of calcium carbonate gives the best maximum availability of both nitrogen and phosphorus so far as the highly acidic (Ranchi) soil is concerned. However, the application of calcium acetate gave the best maximum availability of nitrogen and phosphorus in the slightly acidic (Sarnath) soil (Tables 2 and 3). The lowest position regarding the availability of nitrogen and phosphorus has been generally found with the addition of calcium silicate in both the acidic soils.

The above observations point out that biological processes, like oxidative decomposition of organic matter[8], transformation of nitrogen from ammonia to nitrate and nitrogen fixation which are enhanced in presence of calcium played their dominant role in increasing the availability of soil nitrogen[10,11]. This aerated condition of the soil in presence of calcium is helped by an ample supply of water in the beginning (here treatment B), because of easy movement of calcium at the exchangeable sites. This favoured the growth of different micro-organisms responsible for oxidative decomposition of organic matter that released protein and amino sugar-bound nitrogen mainly in the form of ammonia[9]. Incidentally,

TABLE 2—Changes in the Measure of Available Soil Nitrogen with 8 m.e. of Calcium Salts/100 g. Soil

Calcium Salt Added	SOIL																	
	Ranchi (Bihar)									Sarnath (Varanasi)								
	A			B			C			A			B			C		
	Av. N, ppm	pH I	pH II	Av. N, ppm	pH I	pH II	Av. N, ppm	pH I	pH II	Av. N, ppm	pH I	pH II	Av. N, ppm	pH I	pH II	Av. N, ppm	pH I	pH II
Calcium chloride	120*	5.70	5.40	124	5.75	5.40	102	5.80	5.20	200	6.5	6.3	202	6.8	6.3	195	6.7	6.4
Calcium iodide	105	5.70	5.40	112	5.75	5.30	110	5.80	5.30	205	6.65	6.3	215	6.7	6.35	198	6.8	6.2
Calcium bromide	100	6.00	5.40	115	5.9	5.4	110	5.8	5.2	190	6.5	6.3	195	6.5	6.45	190	6.5	6.2
Calcium acetate	110	5.9	5.5	115	6.00	5.40	113	6.0	5.4	250	7.0	6.85	258	6.65	6.50	250	6.8	6.65
Mono-calcium-phosphate	128	6.2	7.00	130	6.3	6.8	128	7.0	7.4	205	7.0	7.40	208	6.7	6.9	205	8.0	7.4
Calcium oxide	120	6.0	6.2	128	6.4	6.6	119	6.2	6.4	198	6.7	7.00	225	6.95	7.2	205	6.9	7.2
Calcium carbonate	189	6.4	6.9	205	6.5	7.5	195*	6.7	7.2	201	6.8	7.00	211	6.8	7.0	195	6.9	7.0
Calcium sulphate	125	5.75	5.9	125	5.65	5.8	125	5.8	6.0	201	6.8	6.9	200	6.6	6.85	197	6.9	7.00
Calcium Silicate	108	6.00	5.8	110	6.00	5.9	109	6.1	5.8	175	6.65	7.2	191	6.95	7.00	190	6.75	6.8
Control	50	5.10	5.10	54	5.1	5.5	50	5.1	5.2	150	6.4	6.4	154	5.4	6.45	152	6.4	6.5
Fischer's 't' value at 5% level of significance	7.80			6.00			7.27			2.75			2.62			2.66		

Note: 1.*Maximum value of available nitrogen obtained only at 16 m.e. calcium salts per 100 g. soil.
2. I—Initial pH, II—Final pH.
3. The calculated 't' value for 8 d.f. at 5% level of significance = 2.306.

TABLE 3—CHANGES IN MEASURE OF AVAILABLE P_2O_5 WITH 8 M.E. OF CALCIUM SALTS PER 100 G. SOIL

Calcium Salt Added	SOIL																	
	Ranchi (Bihar)									Sarnath (Varanasi)								
	A			B			C			A			B			C		
	Av. P_2O_5, ppm	pH I	pH II	Av. P_2O_5, ppm	pH I	pH II	Av. P_2O_5, ppm	pH I	pH II	Av. P_2O_5, ppm	pH I	pH II	Av. P_2O_5, ppm	pH I	pH II	Av. P_2O_5, ppm	pH I	pH II
Calcium chloride	420	5.70	5.40	450	5.75	5.45	460	5.80	5.20	1120	6.50	6.30	1160	6.80	6.30	1180	6.70	6.40
Calcium iodide	450	6.70	6.40	480	5.75	5.30	500	5.80	5.30	1000	6.65	5.30	1050	6.70	6.35	1100	6.80	6.20
Calcium bromide	350	6.00	5.40	400	5.90	5.40	450	5.80	5.20	1000	6.40	6.30	1050	6.50	6.45	1090	6.50	6.20
Calcium nitrate	420*	5.90	6.10	448	5.85	5.95	580	5.80	5.90	1220	6.60	6.80	1380	6.90	7.40	1400	6.85	7.00
Calcium acetate	350	5.90	5.50	450	6.00	5.40	500	6.00	5.40	1250	7.00	6.85	1410	6.65	6.50	1450	6.8	6.65
Calcium oxide	450	6.00	6.20	450	6.4	6.6	600	6.20	6.40	1150	6.70	7.00	1230	6.95	7.20	1250	6.99	7.20
Calcium carbonate	720*	6.40	6.90	820*	6.5	7.5	880*	6.70	7.70	1120	6.80	7.00	1180	6.80	7.00	1200	6.90	7.00
Calcium silicate	260	6.00	5.80	280	6.00	6.90	200	6.10	5.80	950	6.65	7.20	1000	6.95	7.00	1120	6.75	6.80
Calcium sulphate	440	6.75	5.90	450	5.65	5.80	500	5.80	6.00	1110	6.80	6.90	1200	6.60	6.85	1220	6.90	7.00
Control	200	5.10	5.10	220	5.10	5.15	240	5.10	5.20	700	6.40	6.40	620	6.40	6.45	740	6.40	6.50
Fishcher's 't' value at 5% level of significance	8.90			5.32			5.60			4.00			11.50			15.00		

Note: 1.*Maximum value of soil P_2O_5 obtained only at 16 m.e. of calcium salts per 100 g. soil.
2. I—Initial pH; II—Final pH.
3. The calculated 't' value for 8 d.f. at 5% level of significance—2.306.

it may be pointed out that in the application of calcium acetate, especially the acetate ions are known to favour an enhanced activity of useful bacteria and increase more bacterial decomposition of carbohydrates, amino sugars and animal tissues[12].

Similarly, it may be stated that the increased availability of soil phosphorus with the application of calcium salts must be due to greater mineralization of organic phosphorus[13,14], especially with treatment C (an alternate wetting and drying process) and in presence of calcium carbonate (highly acidic soil) and calcium acetate (silghtly acidic soil). Further, it is generally observed that the decomposition of phosphorus-bearing organic matter or the growth of phosphate-loving organisms is enhanced in presence of nitrate[15] and acetate ions, the latter being more useful in the oxidation of carbohydrates and animal tissues[12].

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The effect of alternate wetting and drying on phosphate retention for a period of 45 days was studied with two phosphate ion species (ortho- and pyrophosphate) in black, red and laterite soils. The increase in phosphorus retention was found to follow the decreasing order: laterite > red > black soils after 45 days. There was an increase of phosphate in aluminium and calcium combinations. However, iron-bound phosphate decreased with pyrophosphate, while no major change was found with orthophosphate. Adsorbed phosphate was found to decrease in both cases.

Effect of Alternate Wetting and Drying on Phosphate Retention

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Introduction

The chemistry of soil phosphorus is much complicated owing to the ability of each phosphate ion to form a multiplicity of compounds of different compositions and variable solubilities. A complete recovery of phosphate from added phosphatic fertilizers by plants has been the object of many studies.

It is generally accepted that under water-logged conditions, aluminium-bound phosphate increases and reductant soluble iron-phosphate decreases[1]. Shelton and Coleman[2] reported that when phosphorus is applied in large quantities to a high phosphate-fixing soil, it gets converted rapidly into aluminium and iron-bound phosphorus. Over a period of eight years a decrease in aluminium-phosphorus with an increase in iron-bound phosphorus occurred. Chang and Chu[3] observed that under water-logged condition, the added phosphate is mostly fixed as iron phosphate. However, Banerjea and Mandal[4] reported that there is a marked increase in aluminium-, iron- and calcium-bound phosphate fractions in all soils, the last two fractions being highest in acidic and alkaline soils respectively.

The present study was undertaken to determine the effect of alternate wetting and drying on phosphate reiention and its distribution using two different phosphate ton species under laboratory conditions with a view to simulate field conditions, where there are definite periods of wetting and drying. From the results a good correlation can be established whereby recommendation of phosphatic fertilizers can be made with profitable use to the cultivators. Further, this type of study will help in understanding the actual phenomenon occurring during rainy season when phosphatic fertilizers are applied to the soils.

Experimental

Surface samples of red, black and laterite soils were used. 5 representative samples of red soils were collected from Mirzapur, Sukrit, Rewa, Panna and Chhattarpur (situated in the region of red soils), whilst black soils were collected from Ballia, Gaipura, Birha, Rewa and Satna districts (all belonging to black soil region). The only laterite soil sample was obtained from Bhubaneshwar (Orissa), where laterites predominate.

Procedure: Some of the chemical constituents of the samples (Table 1) were determined following the method by Jackson. The two phosphate ion species used were ortho (KH_2PO_4) and pyrophosphate ($K_4P_2O_7$). The amounts of phosphate in leachates were determined colorimetrically using sulphomolybdic acid and chlorostannous reagents[5].

1.0 g. of each soil sample was treated with 250 μg (250 ppm) of phosphate in solution form as orthophosphate (KH_2PO_4) and pyrophosphate ($K_4P_2O_7$) separately and shaken for one hour and left overnight. Then filtration was accomplished by using a suction pump.

The amount of phosphate in the filtrates was determined by a colorimetric method. The difference between

TABLE 1—SOME OF THE CHEMICAL PROPERTIES OF SOILS

Soils	pH	R_2O_3, %	$CaCO_3$, %	Organic Carbon, %
Red Soils				
Mirzapur (U.P.)	6.4	5.3	0.87	0.76
Sukrit (U.P.)	7.7	10.0	1.25	0.90
Rewa (M.P.)	6.8	10.28	0.50	0.33
Panna (M.P.)	6.4	9.6	0.20	0.51
Chhattarpur (M.P.)	6.8	6.9	0.30	0.27
Black Soils				
Ballia (U.P.)	8.0	16.72	1.75	0.52
Birha (U.P.)	7.4	17.99	1.25	0.21
Gaipura (U.P.)	7.4	21.88	2.50	0.45
Rewa (M.P.)	8.2	10.76	3.00	0.28
Satna (M.P.)	7.2	13.00	1.50	0.70
Laterite Soil				
Bhubaneshwar (Orissa)	6.0	12.00	Nil	0.28

the amounts of phosphate added and present in the filtrates was taken as the amount retained by the soils. The phosphated soils were fractionated for different inorganic phosphate combination using the procedure by Jackson[5]. The average results of all the three types of soils are shown in histograms (Figs. 1A & 1B and 2A & 2B).

Wetting and Drying Experiments: To 1.0 g. soil samples taken in test tubes, 250 μg. of phosphatic solution was added and the tubes were kept for drying in an incubator around 50°C for 45 days. When the soils dried, they were wetted with 2-3 ml. of distilled water. Thus, the wetting and drying process was repeated 12 times. These soils were then used for fractionating different forms of phosphate as described above. The average results of all the types of soils are shown in histograms (Figs. 2A & 2B).

Results

The results obtained can be arranged under the following two heads:

(1) *Alternate Wetting and Drying with Orthophosphate as Phosphate Source:* The retention of phosphate from orthophosphate (KH_2PO_4) after 45 days showed a trend similar to that obtained for 18 hours. The black soils retained the maximum, while the laterite retained the least amount, the red soils occupying an intermediate position. In black soils, the combination of phosphate was found in following decreasing order: Al - P > Ca - P > Fe - P after 45 days, which is similar to 18 hours' treatment.

The results obtained from red soils and the laterite after 45 days were also similar, i.e. maximum amount of phosphate went into combination with aluminium followed by iron-phosphate, calcium-phosphate and adsorbed phosphate. It is curious that after 18 hours, the order of Al - P and Fe - P was found to be reversed, viz. Fe - P > Al - P > Ca - P > Ad - P in both soils.

(2) *Alternate Wetting and Drying with Pyrophosphate as Phosphate Source*: With pyrophosphate ($K_4P_2O_7$) similar trend of phosphate retention was observed as with orthophosphate for all the soils both after 18 hours and 45 days of alternate wetting and drying. The combination of phosphate in different inorganic forms was found to be similar to that as 18 hours, i.e. Ca - P > Al - P > Fe - P > Ad - P in black soils. However, the results obtained from red and the laterite soils were quite similar to that for orthophosphate, i.e. Fe - P > Al - P > Ca - P > Ad - P after 18 hours and Al - P > Fe - P > Ca - P > Ad - P after 45 days. The comparative average

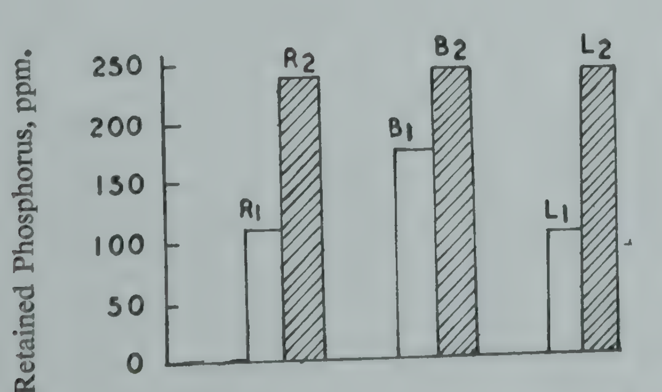


Fig. 1A—Retention of Phosphorus by Different Soils when Potassium Orthophosphate was used as source of Phosphorus

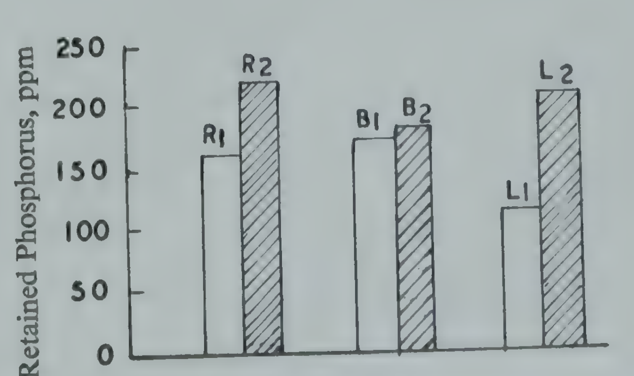


Fig. 1B—Retention of Phosphorus by Different Soils when Potassium Pyrophosphate was used as Phosphorus Source

[$R_1B_1L_1$—Retained Phosphorus after 18 hr. $R_2B_2L_2$—Retained Phosphorus after 45 Days]

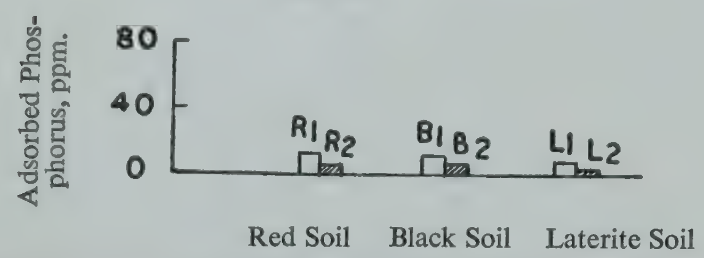
results of red, black and laterite soils are shown in histograms (Figs. 2A & 2B).

Discussion

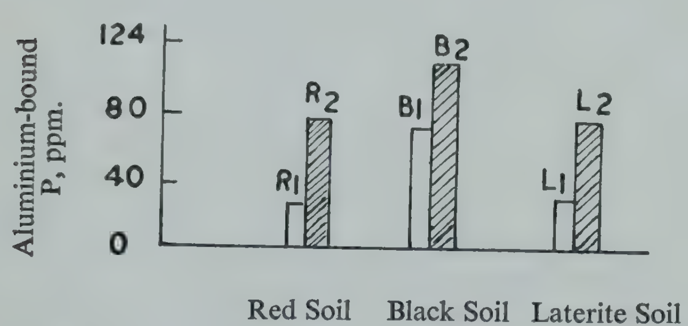
When any soluble phosphate is added to soils, the phosphate ions react with their constituents, such as iron, aluminium and calcium which are supposed to be the most active phosphate-fixers in soils, and thus get retained. The amount of phosphate retained is likely to vary with time and with the alternate wetting and drying cycles. The results show that the retention of phosphate was increased after 45 days of alternate wetting and drying the phosphated soils. It is rather interesting to note that there was a maximum increase in the retained phosphate in the laterite soil followed by red and black soils irrespective of the phosphate ion species.

When the period of contact was much less, viz. 18 hours, and there was no alternate wetting and drying,

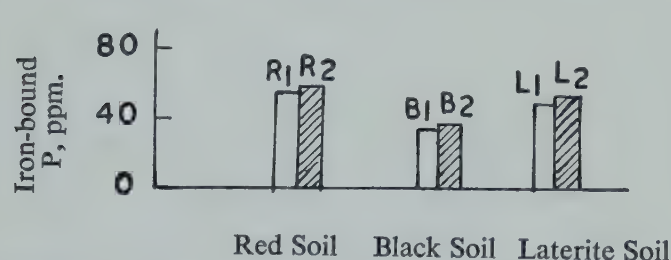
Fig. 2A



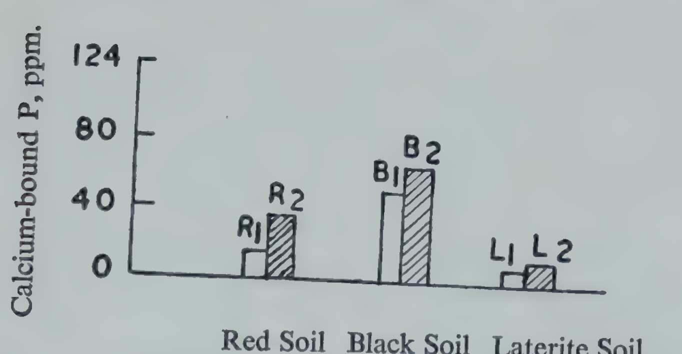
Distribution of Adsorbed Phosphorus of Different Soils When Potassium Orthophosphate was Used as Source of Phosphorus



Distribution of Aluminium-bound Phosphorus of Different Soils when Potassium Orthophosphate was used.

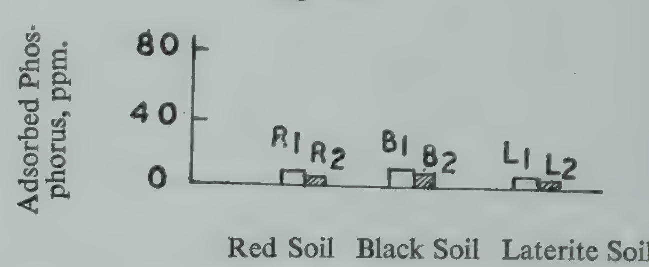


Distribution of Iron-bound Phosphorus of Different Soils when Potassium Orthophosphate was used.

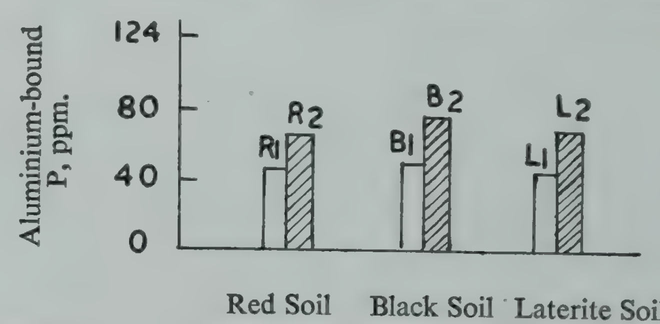


Distribution of Calcium-bound Phosphorus of Different Soils when Potassium Orthophosphate was used.

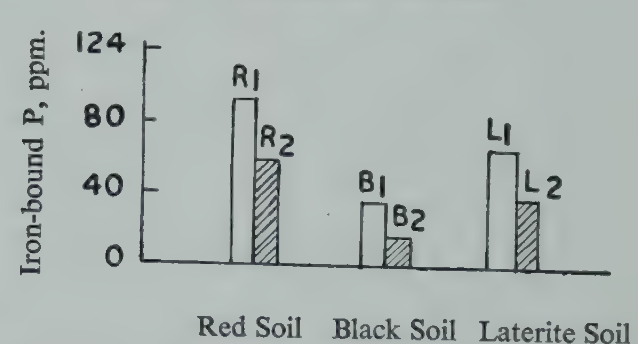
Fig. 2B



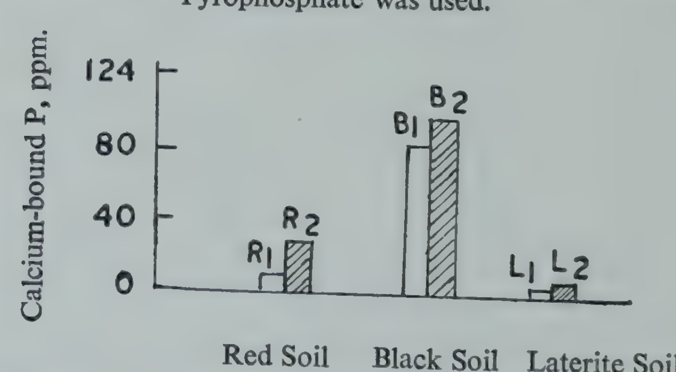
Distribution of Adsorbed Phosphorus of Different Soils When Potassium Pyrophosphate was Used as Source of Phosphorus.



Distribution of Aluminium-bound Phosphorus when Potassium Pyrophosphate was used.



Distribution of Iron-bound Phosphorus when Potassium Pyrophosphate was used.



Distribution of Calcium-bound Phosphorus when Potassium Pyrophosphate was used.

$R_1B_1L_1$—Different Combination of Inorganic Phosphorus after 18 hr.
$R_2B_2L_2$—Different Combination of Inorganic Phosphorus after 45 Days.

the following reverse order in the retention of phosphate was obtained: black soil > red soil > laterite soil (Figs. 1A & 1B).

As a result of wetting and drying, reduction and oxidation cycle may lead to changes in various forms. However, there is a distinct change in iron-phosphate which shows that Fe^{3+} got changed into Fe^{2+} due to water-logged conditions, resulting in a decrease in iron-phosphate. The released ferrous phosphate is likely to get distributed into other forms.

Adsorbed phosphate (Ad - P) was found to decrease in all soil types but a marked increase of phosphate in aluminium combination was found. At the same time, Fe - P decreased with pyrophosphate in all soils but with orthophosphate, a small increase in iron-phosphate was noticed and calcium phosphate increased in all soils.

The alternate wetting and drying simulated in the laboratory may prove helpful in understanding the changes that take place under natural conditions when seasonal changes occur and phosphate fertilization is practiced in a variety of soil types.

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[Original mss. received on Feb. 2, 1971]

A new method has been developed for the gravimetric estimation of choline. The method is quite suitable for the estimation of choline from as low as 0.5 per cent concentration within high limits of accuracy. The method is also suitable for the estimation of choline in the presence of appreciably high amounts of ethylene chlorohydrin.

Gravimetric Estimation of Choline by Hexanitrodiphenylamine

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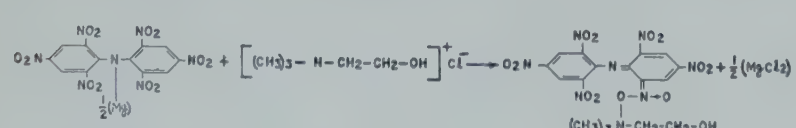
Choline (trimethyl- β-hydroxy ethylammonium hydroxide) $[(CH_3)_3\text{-N-}CH_2\text{-}CH_2\text{-OH}]^+ OH^-$ salts come under the category of quaternary ammonium compounds. Nitrogen in such compounds is pentavalent, possessing four similar covalent bonds and one electrovalent bond. Thus, in a choline salt positively charged cholinium ion $[(CH_3)_3\text{-N-}CH_2\text{-}CH_2\text{-OH}]^+$ and negatively charged cations are connected by means of an electrovalent bond, which is responsible for the ionic character of choline salts.

From the basicity point of view, choline is much more stronger base than magnesium hydroxide; it was therefore thought that the former might replace magnesium from magnesium dipicrylaminate[1] in solution and give rise to a stable choline salt with hexanitrodiphenylamine. Experiments carried out showed positive results and sparingly soluble choline salt, cholinium-dipicrylaminate was obtained. Cholinium-dipicrylaminate was found to be very stable and gave a.m.p. in-between 205-210°C with decomposition. The possible reactions are given below:



Magnesium Dipicrylaminate | Choline Chloride | Cholinium Dipicrylaminate

Solubility of cholinium dipicrylaminate in water at different temperatures was studied and it was found that the solubility of the latter in water, at 25°C was 32 mg./100 ml of water, which confirmed that like potassium[2] and guanidine, choline could also be gravimetrically estimated with hexanitrodiphenylamine.

Procedure of Gravimetric Estimation

For the gravimetric estimation of choline salts (choline chloride in this particular case), a weighed quantity of choline-chloride was taken in a 250 ml. beaker and dissolved in 20 ml. of distilled water. A measured quantity of magnesium dipicrylaminate reagent was gradually added to it with constant stirring of the reaction mixture. Ruby red crystalline precipitate of cholinium dipicrylaminate appeared instantaneously. After complete addition of the precipitant, the reaction mixture was again stirred vigorously for about five minutes and was left for settling at room temperature (25-30°C) for about half an hour. Cholinium-dipicrylaminate was collected by filtration through a G-3 sintered glass crucible under tap suction. It was washed free of the adherent contaminants with saturated solution of cholinium dipicrylaminate three times and finally twice with 5 ml. of ice cold water. The precipitate was dried to constant weight at 100°C and weighed.

Estimation of choline in the presence of ethylene-chlorohydrin was done by addition of a known quantity of choline-chloride to a weighed quantity of ethylene-chlorohydrin and then made the total volume 20 ml. by addition of requisite amount of distilled water. A measured quantity of magnesium dipicrylaminate was followed for the precipitation of choline-dipicrylaminate. The precipitate was filtered and dried as before.

Discussion

Factors for calculating weight of choline and choline-chloride from a known quantity of cholinium-dipicrylaminate are calculated to be 0.2231 and 0.2574 respectively. For complete precipitation of choline as cholinium-dipicrylaminate, precipitant (maxan) added was 10 per cent more than what was stoichiometrically required. In almost all such cases precipitation of cholinium dipicrylaminate obtained was found to be 99 per cent of the theoretical value. However, in cases, where concentration of choline-chloride was under 1 per cent, the estimated values were between 98.2-99.81 per cent. Concentrations higher than 6 per cent weight/vol. were not tried due to bulkiness of the precipitate. Ideal repeatable results were obtained, when the concentration of choline-chloride in solution was between 1 and 4 per cent. Settling time up to 3 hours did not show any change in the yield. The estimated values of cholinium dipicrylaminate precipitated in the presence of ethylene-chlorohydrin (varying from 1 to 9 per cent), were in-between 99.52-99.41 per cent, showing a slight decrease in the precipitate on increasing the concentration of the ethylenechlorohydrin in the reaction mixture.

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[Original mss. received on Aug. 8, 1970]

The effect of ammonia synthesis gas has been studied on the materials of construction of two ammonia converter baskets. In one case, extensive nitriding of AISI 347 stainless steel was observed after 14 years' service. The mild steel heater rods suffered decarburization and developed microcracks in about 4 years. In another case, heater rods made of stainless steel equivalent to AISI 430 fractured only after about 10,800 hours' service.

Attack of Ammonia Synthesis Gas on Steels: Case Studies

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CASE 1

During the annual maintenance of an ammonia plant, the catalyst basket, the insulation-holding jacket and heater rods were subjected to a detailed examination. Synthesis gas mixture (composition in per cent: N_2-20, H_2-60, NH_3-12 and inerts 8) at a pressure of about 5000 lbs/sq.in. and 500°C flowed through the baskets. The material of construction of the catalyst basket and the insulation-holding jacket was AISI 347 type of stainless steel and the heater rods were made of mild steel. For detailed examination, two used baskets were selected—one run for 17 months and the other for 149 months—and compared with a new basket.

New Basket and the One Run for 17 Months

Visual examination of the two baskets showed no

apparent rusting of the surface or any other defect. Except for the weld metal the two baskets were non-magnetic. The metallographic structures of the base metal of both the inside and outside surfaces were identical and were austenite with fine carbide precipitation throughout. The weld metal in both the baskets had dendritic structure with pools of ferrite. The hardness of both the inner and outer surfaces was identical and in the range 190-195 BHN.

Catalyst Basket in Service for 149 Months

Visual examination of the basket showed deep pitting and rusting throughout the inside as well outside surfaces, especially at the lower portions. In the top portion, the insulation-holding jacket also appeared severely corroded and pitted and had numerous cracks. The entire basket was found to be magnetic, the extent being different at different locations; the maximum effect was on the inside surface.

Metallographic examination revealed nitriding of the inner surface of the basket. The maximum depth of nitriding was 0.5 mm (Fig. 1). Next to the nitrided layer the structure was austenitic. In the austenite matrix some dark etching phase also appeared (Fig. 2). The nitrided layer was strongly magnetic and extremely hard. The hardness of the inner nitrided layer was 460 BHN and that of the outer surface 195 BHN.

The insulation-holding jacket was also highly magnetic and extremely hard. It was severely pitted throughout the surface (Fig. 3). Its metallographic examination showed extensive nitriding on both the inside and outside surfaces with multiple cracking (Fig. 4). At certain portions the entire plate had become nitrided (Fig. 5).

Heating Elements

The present practice is to replace the old heating elements with new ones at the time when the catalyst basket is opened up, which is done after about every four years. To study the effect of synthesis gas on the heating rods, their compositions were determined and metallographic examinations were carried out. The used and unused heating rods had the following compositions.

	Unused rod	Used rod
C	0.12	0.04
Mn	0.41	0.42
Cr	0.22	0.23

Metallographic examination revealed the structure of both the used and unused rods to be identical, i.e. ferrite pearlite. The used heating rod showed severe decarburization and microcracks (Figs. 6 and 7). The microcracks were more extensive near the outer region.

Discussion

The present study indicates that AISI 347 type stainless steel is susceptible to nitriding under the operating conditions of ammonia converter. The nitrided layer was highly magnetic and extremely hard. This appeared to be a time effect since no nitriding could be observed in the basket run for 17 months, whereas the effect was marked in that run for 149 months. In the case of insulation-holding jacket, nitriding had occurred on both the sides, since both the inside and outside surfaces come in contact with the synthesis gas.

Nitriding of the surfaces of stainless steel have been reported in literature[1-3]. Ihrig[1] has stated that the attack of synthesis gas mixture on stabilized steels is minimum but has advised that such steels should be checked for nitriding at regular intervals if the attack has been progressive. Hughes[4] has also observed the dark etching phase present in the austenite matrix and reported it to be complex nitride, but no detrimental effect of this phase has been reported.

Analytical composition and metallographic studies have indicated clearly that the mild steel heating rods have suffered decarburization resulting in development of microcracks during service. This could be explained as being caused by reaction of atomic hydrogen with carbon forming methane, the atomic hydrogen itself being formed by the dissociation of ammonia at the steel surface. This methane becomes accumulated in the interior grain boundaries. This exerts a great pressure on the grains and the gas finally escaping cause microcracks and decarburization.

CASE 2

In another catalyst basket, some heater rods were found broken at one end and had fallen inside the converter basket after it was in service for only about 10,800 hours. Attempts to unscrew at the other end for the removal of rod caused fracture of the rod end. Subsequently, during handling, one of the rods was broken on striking with another object. Synthesis gas of composition (in per cent), N_2-24, H_2-73.6 and NH_3-2.4, at 520°C and 365 kg/cm^2 pressure passed through the basket. The material of construction of the heater rods was equivalent to AISI-type 430 stainless steel.

Visual examination revealed a dark adherent, hard

[All figures except Figs. 3 and 8 are reduced to ⅔rd size.]

Fig. 1—Transverse Section of the Parent Metal Showing its Austenite Structure and Inner Nitrided Layer ($\times 200$)

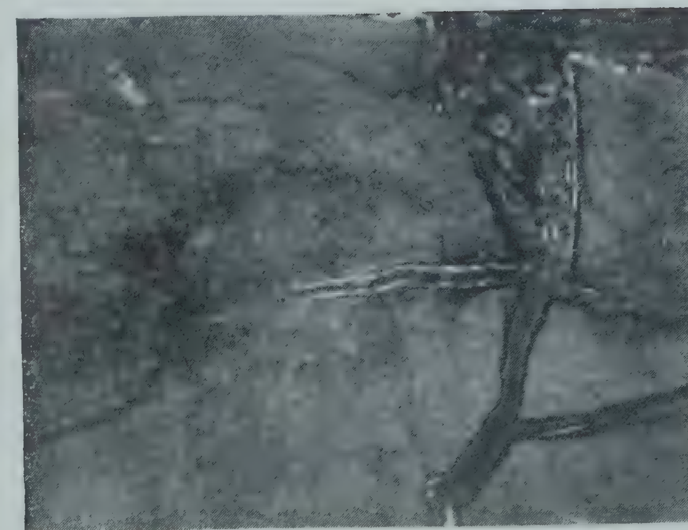

Fig. 4—Nitrided Layer with Multiple Cracking—Dark Field Illumination ($\times 120$)

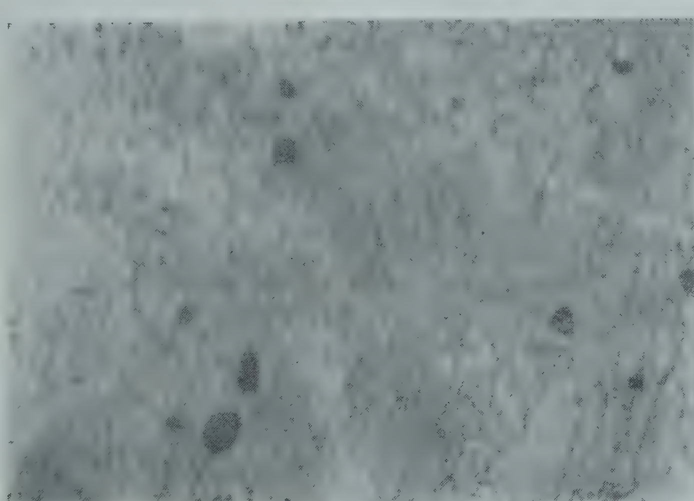

Fig. 2—Transverse Section of the Parent Metal Showing its Austenite Structure and Dark Etching Phase in the Matrix ($\times 340$)

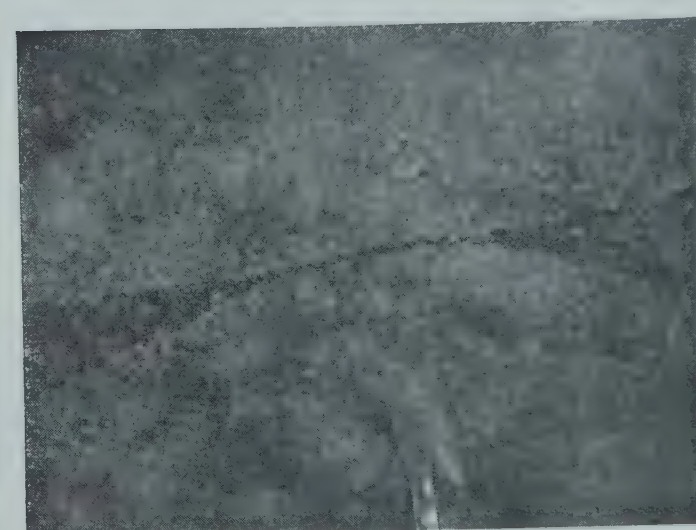

Fig. 5—Parent Austenite Matrix Present as Narrow Band Surrounded by the Nitrided Layer—Dark Field Illumination ($\times 120$)

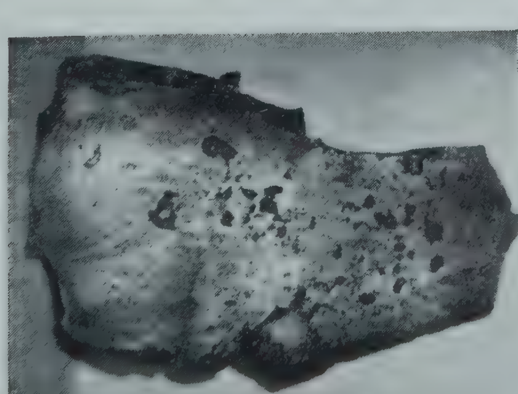

Fig. 3—Insulating Holding Jacket Plate Showing Extensive Corrosion and Pitting
[Reduced to $^3/_5$th size]

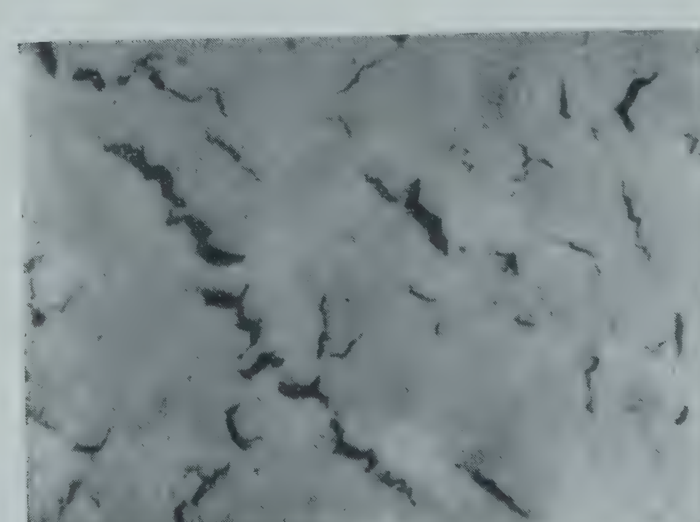

Fig. 6—Used Rod in the Unetched Condition Showing Micro-cracks ($\times 120$)

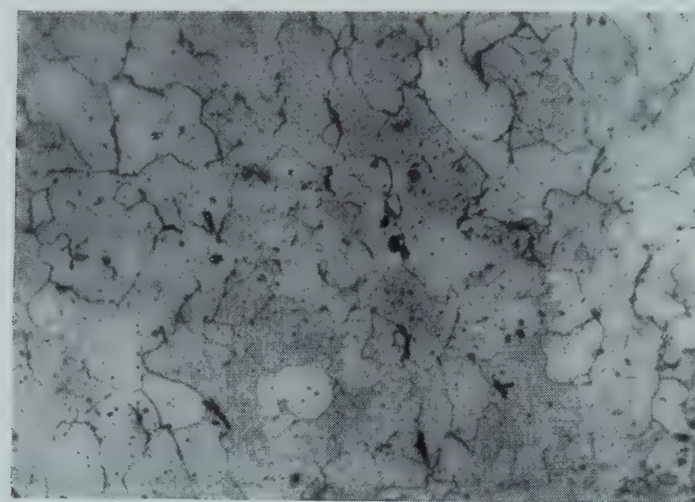

Fig. 7—Used Rod Showing the Ferrite-Pearlite Structure and Microcracks in the Structure ($\times 340$)

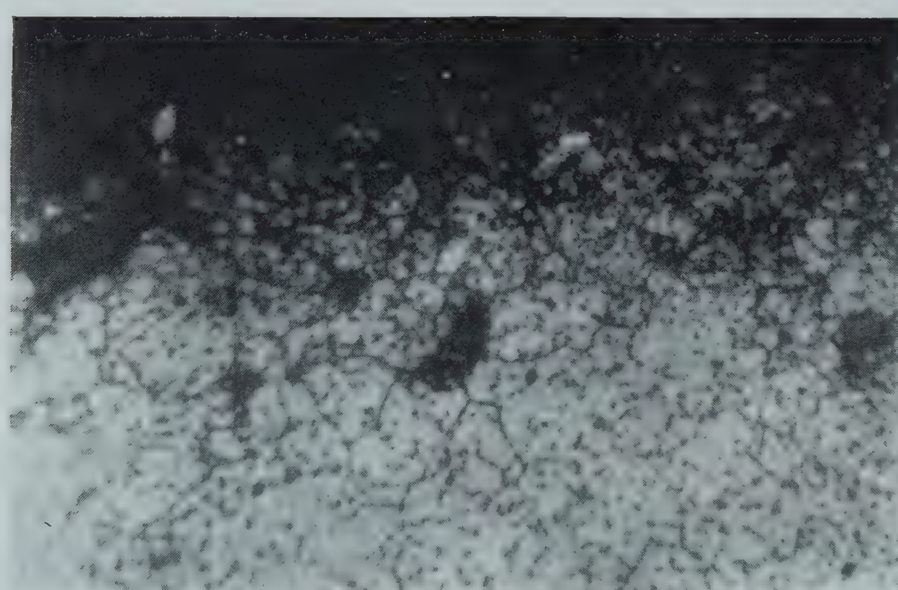

Fig. 8—Rod Showing Ferritic Structure of the Inner Core, the Outer Nitrided Case and the Grain just Adjacent to the Nitrided Case Showing Inward Progress of Nitriding ($\times 340$)

coating on the outer surface. The heating rod was found to contain 16.9 per cent chromium. Mechanical tests gave the following results.

Outer case	
Hardness	477 BHN
Inner core	
Hardness	240 BHN
U.T.S.	51.3 tons/sq. in.
Elongation	24 per cent
Reduction in area	45 per cent

Metallographic examination revealed the structure to be ferritic with precipitated carbide. A nitrided case (Fig. 8) was present on the outside surface, the thickness of the case being 0.5 mm. maximum. Just adjacent to the outermost nitrided case the grains, though ferritic, showed inward progress of nitriding.

Discussion

The analytical composition and structure of the inner core are typical of the AISI 430-type stainless steel, but extensive nitriding had occurred on the outermost layers and the high hardness of the outer case is due to nitriding. The mechanical properties of inner core are also affected to some extent by the inward progress of the nitriding as indicated by slightly lower values of tensile strength. elongation and reduction in area and increased hardness, This type of material, though intended for high temperature service, has suffered nitriding in the environment of ammonia converter because of its strong tendency to form nitride.

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[Original mss. received on March 21, 1971]

Urea reacts with monocalcium phosphate monohydrate to form an adduct and releases water of crystallization. This reaction has been studied under various conditions. Addition of a small amount of moisture is necessary to initiate the reaction although the increase of initial moisture content is without any significant effect on the ultimate release of the water of crystallization. The extension of the period of mixing leads the reaction to completion and increase of temperature enhances the release of water. Various additives also influence the reaction in a marked way.

A Study on the Urea-Monocalcium Phosphate Adduct Formation

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Bulk blends of urea and TSP lose their free-flowing characteristics rapidly[1]. This rapid deterioration of the product has been attributed to the urea-monocalcium phosphate (MCP) adduct formation and consequential release of water of crystallization according to the following equation[2].

$$Ca(H_2PO_4)_2\,H_2O + 4CO(NH_2)_2 = Ca(H_2PO_4)_2\,4CO(NH_2)_2 + H_2O$$

The released water dissolves urea and because of the high solubility of urea there is a considerable increase in the liquid phase, which causes the blend to become wet and sticky. The water-soluble phosphate-carrier in both normal and triple superphosphates consists exclusively of MCP monohydrate. The adduct formation is fairly rapid and is completed within 90 min[3].

In the present study, the extent of release of water of crystallization, which indicates the extent of adduct formation as a result of mixing pure MCP monohydrate with urea, has been estimated. The influence of added moisture on the extent of adduct formation has been noted. The effect of the presence of some of the fertilizer materials on it has also been studied.

Experimental

Reagents: All the reagents were of AnalaR grade. MCP monohydrate was of Riedel-de-Haenag-make and urea of BDH AnalaR grade. The reagents used were powdered (—30 mesh) in an agate mortar and dried over a sulphuric acid desiccator.

Procedure: 1 g. each of urea and MCP monohydrate were weighed into small *petri* dishes and allowed to absorb moisture in a water desiccator. After mixing, the mixture was taken in a small test tube (2.5 cm. diam., 6 cm. height). The test tube with its content was then fastened to the stem of a gas-bubbling jar, which was kept in a thermostatic water-bath (accuracy 0.1°C). Air, dried by passing it through three sulphuric acid jars and a fused calcium chloride tube, was allowed to drive out the moisture released in the reaction by means of a water pump. The sample tube was taken out from time to time, cooled and weighed. After heating in this way for 20 hours, the tube was kept in an evacuated desiccator containing sulphuric acid (conc.) at 30 $\pm$ 2°C. The tube was weighed till the last two weights were constant.

Results and Discussion

Lundstrom and Whittaker[4] found that the hydrolysis of urea is a function of moisture content and the extent of urea hydrolysis is maximum when the water content is high, viz. 1 to 2 mole of H_2O/mole of urea. They also found that any further increase of water from 2 to 15 moles did not have any appreciable effect on the hydrolysis of urea. In order to avoid this complication, the maximum water/urea mole ratio was kept as low as 0.16, in which case the hydrolysis of urea can be neglected.

In the present work, it has been shown that dry MCP monohydrate and urea do not react and a liquid phase appears to be necessary to initiate the adduct formation. This confirms the finding of Frazier *et al*[2]. The reaction seems to proceed slowly in presence of moisture (Table 1).

TABLE 1—EFFECT OF MOISTURE ON UREA-MCP MONOHYDRATE AND UREA REACTION

[Temp. 40°C; Molar ratio: 4.2 :1; Time—7 days]

Moisture Added*, %	Water of Crystallization Released, %
1	79.0
2	81.1
3	83.9
4	87.5
5	87.6

*The percentages are on the basis of urea added.

The release of water of crystallization was determined by passing completely dry air through the sample maintained at 40°C in the thermostat except when the effect of temperature was studied. Thus, water released on account of adduct formation was taken up by dry air at the elevated temperature, viz. 40°C. Prior to this, urea and MCP monohydtate, both in powdered form, were kept together for varying periods of time. Fig. 1 reveals

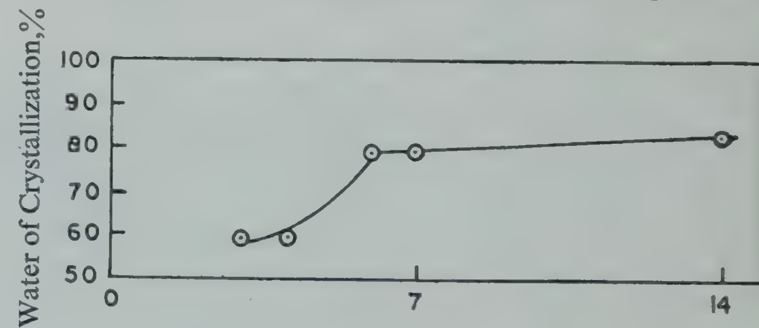

Fig. 1—Release of Water of Crystallization with Different Periods of Storage.
[Urea-MCP Monohydrate Ratio 4.2: 1, Temp. 40°C, Moisture 1 per cent]

the extent of release of water of crystallization with different periods of storage of urea-MCP. The release of water of crystallization (as shown in the figure) increases slowly with the samples stored upto seven days and then remains practically constant. This shows that the adduct formation is apparently complete when the samples are stored for seven days. This is, however, not so as the limit is reached when nearly 80 per cent of water of crystallization is released.

The non-completion of the adduct formation or the consequential release of water of crystallization may be due to the fact that some dicalcium phosphate (DCP) is always formed and precipitated when MCP is dissolved

in aqueous media. The precipitation of dicalcium phosphate dihydrate may act as a buffer to prevent further adduct formation. Moreover, two molecules of water are removed from the system to form dicalcium phosphate dihydrate, thereby reducing slightly the extent of adduct formation.

The effect of increase of temperature appears to increase the release of water of crystallization as is shown in Table 2.

TABLE 2—EFFECT OF TEMPERATURE ON UREA-MCP+1% MOISTURE

[Time—7 days; Molar ratio 4.2:1]

Temperature, °C	Water of Crystallization Released, %
40	79.0
50	85.0
60	88.4
80	94.5

The results (Table 3) indicate that in presence of sulphates of ammonium and potassium, the extent of adduct formation is considerably less than in the case of pure MCP-urea system. This is understandable as in presence of these salts the available calcium in solution phase is reduced due to the formation and precipitation of gypsum ($CaSO_4.2H_2O$) even though calcium sulphate dihydrate is also known to form adduct with urea. In the case of diammonium phosphate, calcium ion is removed from the system as dicalcium phosphate dihydrate. It appears that the extent of adduct formation in a given period of time is dependent on the availability of MCP and urea in the liquid phase. As urea is highly soluble, the rate ultimately depends on the availability of MCP in the solution phase. It is known that solubility of MCP increases in presence of ammonium nitrate[5]. Therefore, the increase in the extent of adduct formation in presence of ammonium nitrate is understandable.

TABLE 3—INFLUENCE OF ADDITIVES ON THE RELEASE OF WATER OF CRYSTALLIZATION

[System: Urea-MCP + 1% moisture; Temp. 40°C; Molar ratio 4.2:1]

Additives	Amount, %	Release of Water of Crystallization, %
$(NH_4)_2SO_4$	22.9	25.9
K_2SO_4	23.2	35.3
$(NH_4)_2HPO_4$	2.6	59.5
$NH_4H_2PO_4$	2.6	79.08
NH_4NO_3	8.9	88.18
None	—	79.0

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[Original mss. received on April 17, 1971]

Investigations on the raw surface waters in the Korba region carried out during April 1964 to March 1965 revealed that the *Hasdeo* river and *Dhengur nala* waters are very soft having very low alkalinity, sulphate, chloride and dissolved solids contents but moderately high in silica. The low mineral content of these waters has certain inherent advantages and disadvantages. The main advantage is the low cost involved in their demineralization. The primary disadvantage is their high corrosivity requiring adequate treatment with lime or alum and lime in a conventional clarifier/softener to make them suitable as industrial cooling water or for domestic use.

The Characteristics of the Raw Waters of *Hasdeo* River and *Dhengur Nala* at Korba (M.P.)

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A site on the left bank of the *Hasdeo* river near the present Korba township in Bilaspur district (M.P.) was selected in 1963 for a coal-based fertilizer factory. The place has several favourable factors, like ready availability of coal and power and a suitable source of water from the *Dhengur nala*, a perennial rivulet flowing across the north of the proposed site terminating into the *Hasdeo* river 7-8 miles downstream. Since the flow of the *Dhengur nala* during the summer season was not considered sufficient to meet the total water requirement of the factory and its township, a feeder channel connecting the *Hasdeo* river barrage pond and the nala to augment the water flow through it was proposed.

As the available data were too meagre to suggest a proper water treatment method, it was felt necessary to undertake a year-round investigation on the characteristics of the two principal sources of water of the region, viz. the *Hasdeo* river and the *Dhengur nala*. The present note gives the principal characteristics of the two raw water sources as obtained from the above investigation.

Materials and Method

Raw water samples were collected from the above sources at predetermined sampling points (Fig. 1) at regular intervals and tested for turbidity, pH and free carbon dioxide content in the field laboratory. The detailed analyses[1] were done in the research laboratory at Sindri.

Results and Discussion

The monthly average data (Tables 1 and 2) for

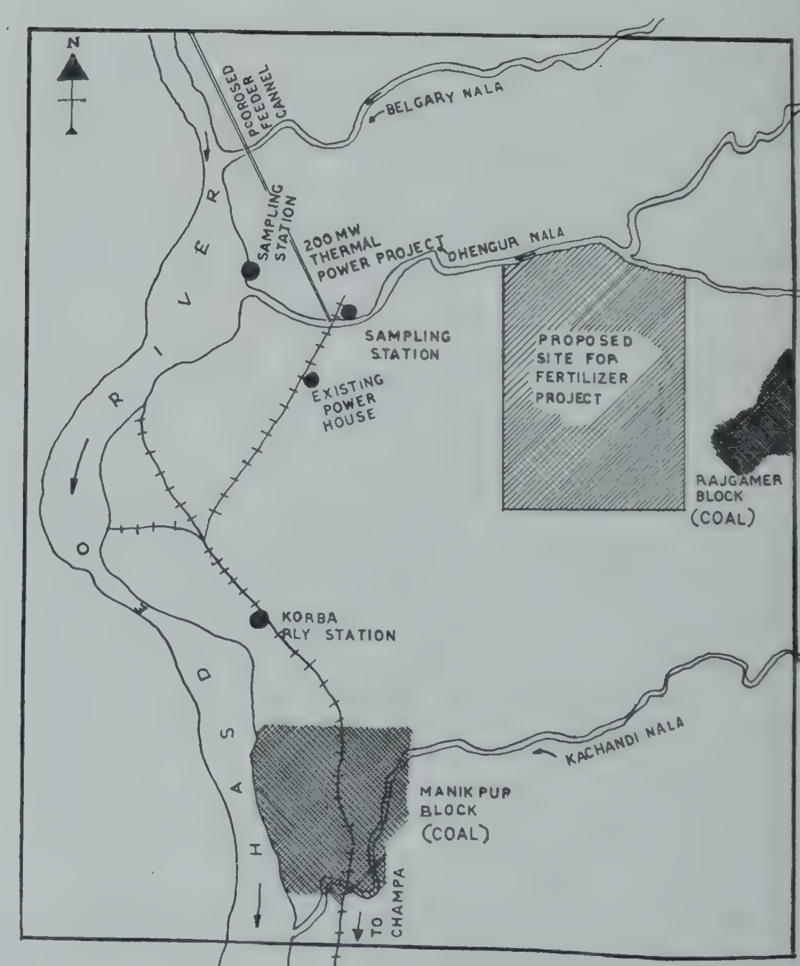

Fig. 1—Location of the Hasdeo River and Dhengur *Nala* near Korba (M.P.)

TABLE 1—CHARACTERISTICS OF THE *Hasdeo* RIVER WATER* IN DIFFRENT MONTHS OF 1964-65

	Analyses† (except otherwise stated), mg/l.												Saturation Index
	Turbidity, Unit	pH	Free CO_2	Alkalinity as $CaCO_3$		Hardness as $CaCO_3$			Chloride as Cl	Sulphate as SO_4	Silica as SiO_2	Dissolved Solids	
				P	M	Ca	Mg	Total					
April, 1964	7	7.5	2.7	0	46	21	13	34	2.0	0.3	23	72	−1.2
May, 1964	10	7.3	4.3	0	49	24	13	37	2.3	0.5	25	76	−1.3
June, 1964	578	7.3	3.4	0	35	18	12	30	2.3	0.3	17	63	−1.6
July, 1964	476	7.0	4.5	0	26	12	9	21	2.8	0.5	14	49	−2.2
August, 1964	746	7.2	4.3	0	32	17	9	26	2.7	0.7	16	62	−1.8
September, 1964	465	7.2	3.2	0	34	13	9	22	1.9	1.0	15	67	−1.9
October, 1964	145	7.6	2.3	0	46	22	10	32	1.5	0.6	17	78	−1.1
November, 1964	68	7.7	2.7	0	52	26	13	39	1.8	0.6	18	83	−0.9
December, 1964	80	7.5	3.5	0	50	25	17	42	1.9	0.5	21	82	−1.3
January, 1965	15	7.4	4.1	0	46	22	15	37	1.9	0.5	20	72	−1.5
February, 1965	12	7.4	3.7	0	44	22	15	37	1.8	0.3	20	64	−1.6
March, 1965	10	7.3	4.3	0	41	20	13	35	1.7	0.4	22	74	−1.7

*Sampling station was a point just above the confluence of the *Dhengur nala* and the *Hasdeo* river
†Monthly average figures.

TABLE 2—CHARACTERISTICS OF THE *Dhengur Nala* WATER* IN DIFFERENT MONTHS OF 1964-65

MONTHS	Analyses† (except where otherwise stated), mg./l.												Saturation Index	Flow, cusecs
	Turbidity, Unit	pH	Free CO_2	Alkalinity as $CaCO_3$		Hardness as $CaCO_3$			Chloride as Cl	Sulphate as SO_4	Silica as SiO_2	Dissolved solids		
				P	M	Ca	Mg	Total						
April, 1964	10	7.1	3.8	0	26	8	7	15	2.2	Trace	24	57	−2.3	72.4
May, 1964	7	7.0	5.1	0	27	10	8	18	2.8	0.5	25	66	−2.3	27.7
June, 1964	270	6.9	6.1	0	28	11	9	20	2.8	1.0	21	62	−2.3	12,5
July, 1964	128	6.7	6.8	0	16	7	4	11	2.0	1.5	17	44	−2.9	1815.0
August, 1964	122	6.8	4.1	0	18	7	4	11	1.6	0.5	19	45	−2.9	2053.0
September, 1964	135	6.9	3.7	0	17	6	5	11	1.2	Trace	16	45	−2.9	1947.0
October, 1964	45	7.0	4.5	0	17	6	5	11	1.3	-do-	16	46	−2.8	547.0
November, 1964	9	7.0	5.5	0	20	7	5	12	1.3	-do-	18	51	−2.7	347.0
December, 1964	7	6.9	5.4	0	19	8	5	13	1.4	-do-	20	48	−2.8	260.0
January, 1965	8	6.9	5.4	0	19	6	7	13	1.3	-do-	20	45	−2.8	188.0
February, 1965	8	6.9	5.4	0	19	7	6	13	1.4	-do-	20	51	−2.6	140.0
March, 1965	9	7.0	4.5	0	21	8	6	14	1.7	-do-	23	54	−2.5	98.0

*Sampling station was near the railway bridge crossing.
†Monthly average figures.

1964-65 indicate that the raw waters from both the sources, viz. *Hasdeo* river and *Dhengur nala* are very soft and more or less similar in nature having exceptionally low alkalinity and dissolved salts content but high in silica; both are very low in chloride and still lower in sulphate contents and free from non-carbonate hardness. Turbidity too remains very low throughout the year except during June to September. From these aspects, both the waters can be classified in the very soft water class with moderately high silica—typical of the rainfed waters of the sandstone regions.

The *Dhengur nala* water differs from that of *Hasdeo* river only in the degree of softness and mineralization, the former containing much lower hardness, alkalinity

and dissolved solids. The maximum figures for hardness, alkalinity and dissolved solids in the latter were found to be 42, 52 and 82 mg/l respectively, while the same for the *Dhengur nala* water were 20, 28 and 66 mg/l (Tables 1 & 2).

The above waters have certain inherent advantages and disadvantages for industrial and domestic uses. For such industries where the need is for partially or fully demineralized waters, these are quite useful, since the total cations and anions are low and the cost for demineralization would invariably be very low. The main disadvantage of these type waters is their high corrosivity which is evident from their saturation index values (Tables 1 & 2).

To utilize these waters for process cooling or domestic use they must be given proper lime or lime and alum treatment in the conventional clarifier/softener for eliminating or reducing their corrosivity by raising their pH, alkalinity and calcium content. The merits of such waters definitely outweigh their demerits, and it is felt that these waters can satisfactorily serve a coal-based fertilizer factory, at Korba.

Acknowledgement

Thanks are due to Sri S. R. Seshan, the then Chief Project Officer, Korba Fertilizer Project, who had kindly extended assistance during this investigation.

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1. *Standard Methods for the Examination of Water, Sewage and Industrial Wastes*, 10th Ed. (Amer. Public Health Assn. Inc., New York), 1955.

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A method has been developed for estimation of impurities in water-immiscible organic liquids using aqueous standards employing an inverted Y-shaped double capillary[1,2] (DCS). Calibration curve is obtained by aspirating the aqueous standards and organic liquid blank simultaneously through two lower ends of DCS. Similarly, organic samples and water were aspirated simultaneously. The concentration values, thus obtained, were corrected for the viscosity of the sample. Alternatively, it is possible to determine the viscosity of the organic liquid, containing known amounts of analyzable elements, by atomic absorption spectrophotometry (AAS).

Use of Aqueous Standards for Estimation of Impurities in Water-Immiscible Organic Liquids by Atomic Absorption Employing Double Capillary

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Introduction

In the analysis by flame methods, if accuracy of high order is required, the standards should be prepared to match with the samples. Most of the analyses by atomic absorption spectrophotometry (AAS) are generally done in very dilute aqueous samples and therefore, simple aqueous standards are commonly employed. Sometimes standard addition method is also used for elimination of matrix difference.

Organic liquids affect the aspiration rate, drop size

and flame condition due to their properties, such as viscosity, surface tension and heat of combustion, etc. These factors influence the absorption greatly and as such, for estimation of impurities in organic liquids, the standards should exactly match with the samples. For samples miscible with water, simulated standards can be easily prepared by mixing them with the aqueous standards. In case of water-immiscible organic liquids, like petroleum products, aqueous standards cannot be prepared. For determination of impurities and additives in gasoline[3–5], cracking feedstock,[6] lubrication oils[7–8] etc., generally standards of metallo-organic compounds, prepared from soluble naphthanates[9] and sulphonates, are used.

In this laboratory, cracking feedstocks are often analysed for iron, vanadium, nickel and copper, which are supposed to have adverse effect when deposited on the catalyst resulting in reduction in its activity[10–11]. In the petroleum industry also, these trace impurities have deleterious effect on certain processes as they alter the distribution of the cracked products[10], therefore their determination is necessary.

For want of metallo-organic standards, the petroleum samples were ashed and the ash was either spectrographically analysed or taken into a solution for analysis by AAS. The ashing procedures are lengthy and cumbersome. In the dry ashing procedure[11], there is a loss of ash and so this method is not very accurate. The metallo-organic standards are not very stable; moreover, they are very expensive and only few firms can supply them.

To overcome the above difficulties, a simple method for estimation of these impurities has been developed by AAS using a Y-shaped double-capillary aspiration system (DCS)[1,2], designed in this laboratory, and used for titration by AAS, multiple standards, addition standards and removal of interferences, etc. Recently, a similiar type of Y-shaped capillary has been used by Leiritie and Mattson[12] for addition of the sample.

Experimental

(a) *Instrument:* A Perkin-Elmer model 303 atomic absorption spectrophotometer, equipped with a standard air-acetylene burner head, hollow cathode lamps and automatic recorder read-out accessory was used. In conjunction with the accessory, a Servo-riter II recorder was used. A double capillary of equal arms [DCS (1:1)][1,2] was employed throughout.

The DCS (1:1) was made as earlier[1]. A hypodermic needle (No. 22) was suitably cut and two 5″ long polythene tubings were fixed to the push-fit plug to form lower ends. A 1″ long tubing was used to connect the needle to the nebulizer.

(b) *Preparation of Standards & Samples:* Aqueous and alcoholic standards were prepared from 1 per cent Harleco standard solutions by successive dilution. Iron standards in methyl iso-butyl ketone (MIBK) was prepared from NBS Tris (1-Pheny1-1, 3-butanediono) iron (III). Copper is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted[9] in MIBK. Similarly, a MIBK blank was prepared. The copper concentration is so adjusted that in the extractant, concentration of copper was 4 μg/ml. Seven naphtha samples were taken and diluted 1:5 with MIBK.

(c) *Procedure:* The standard procedures were adopted, as suggested in cook-book[13], for selection of lamp current, wave length etc. To compensate the enrichment of the flame due to organic liquid, the acetylene flow was reduced until the flame just lifts off the burner. The observations were taken 4 mm above the burner head for studying the effect of organic liquids (Table 1). For other studies, parameters were optimized. DCS (1:1) was used throughout the present experiment. Zero of the instrument was always adjusted by aspirating the blanks simultaneously through the two lower arms of DCS. Naphtha was analysed with the help of a recorder using the noise supression at 4 and scale expanded ten times. The blank was run for one min. in-between the samples. The viscosity values at temperature nearest to the room temperature (24.5°C) were taken from literature[14]. For methanol, ethanol, MIBK blank and naphtha working sample, the viscosities were determined by the Ostwald viscometer.

Results and Discussion

(1) *Effect of Miscible and Immiscible Organic Liquids on Aqueous Standards*: Miscible organic solvents are widely used to enhance the sensitivity. The enhancement in absorption signal of 2 to 5-fold is commonly achieved, which has been established by many workers[15–18] employing a conventional single capillary. This enhancement is due to more transportation of sample and increased efficiency of atomization, which is ascribed to physical properties, like viscosity, surface tension, heat of combustion, etc. Water-immiscible solvents as extractant are also currently in great use in conjunction with flame techniques for spearation of an element or a group of elements of interest from the martix. This generally improves the analytical sensitivity and accuracy. An enhancement of 2 to 5-fold is also achieved with these liquids. The effect of water-immiscible liquids, as such, on aqueous standards has not been studied by a single capillary because they

cannot be mixed with water and form separate layers. This study has been made possible[2] with the use of DCS.

With the help of DCS, the effect of both miscible and immiscible organic liquids on the aqueous sample has been studied by aspirating the sample through one arm of inverted Y-ends and the miscible or immiscible solvents through the other. The effect of a number of organic liquids on 4μg/ml of copper has been shown in Table 1. When only an aqueous copper standard is aspirated through one end and water through the other, the absorption due to 4μg/ml of copper is virtually due to only 2μg/ml of copper because a sample through one end of DCS (1:1) is diluted in the ratio of 1:1. When different organic liquids are aspirated instead of water (Table 1, column 3b), the content of copper in aqueous-organic mixture, reaching the flame, will be different due to viscosities (dealt afterwards), and so the absorbance is normalized for 2 μg/ml of copper for all cases (column 6). The table is divided into three categories, viz. miscible, partly miscible and immiscible liquids and the enhancement due to organic liquids of all the three categories—if the percentage of the organic liquids is considered—is of the same magnitude as expected with these organic liquids. Ketones are known to give the maximum enhancement of signal. Though acetone, methyl ethyl ketone (MEK) and MIBK fall in three different categories (Table 1), the enhancement by all of them is about three times, which is higher than others. MEK and MIBK are partly miscible and immiscible respectively but their overall effect is like that of acetone. It has also been found that the immiscible solvents in conjunction with aqueous samples do not give fluctuation in absorption reading. This is probably due to the homogeneous suspension, which is formed at the junction of the DCS and when nebulized, form smaller drop size than the water alone in the premix chamber.

(2) *Viscosity Effect on Absorption (DCS)—(a) Miscible Liquids*: Viscosity affects the aspiration rate of

TABLE 1—Effect of Organic Liquids on 4 μg/ml. of Aqueous Copper Solution, Employing DCS (1:1)

1	2	3		4	5	6	7	8
Sl. No.	Solubility of Organic Liquid in water	DCS (1:1) a: Left Arm (4 μg./ml. aqueous Copper Solution)	DCS (1:1) b: Right Arm (Organic Liquids)	Absorbance (A)	Viscosity[14] Nearest to Room Temperature, cs.	Normalized Absorbance for 2μg./ml.*	Enhancement**	Organic Liquid Fed in the Flame, %
1.	Miscible liquids	Cu solution	Water	0.1152	1.00	0.1152	1.00	—
2.		,,	Methanol	0.1669	0.59	0.2225	1.93	62.9
3.		,,	Ethanol	0.2041	1.68	0.1627	1.41	37.3
4.		,,	Iso-Propanol	0.2526	2.20	0.1837	1.59	31.3
5.		,,	Acetone	0.1844	0.31	0.3888	3.37	76.4
6.		,,	Pyridine	0.1746	0.88	0.1863	1.62	53.2
7.		,,	Glycerol	0.2147	777.6	0.1073	0.93	0.13
8.		,,	Butyl cellosolve	0.2708	3.05	0.1811	1.57	24.7
9.	Partly Miscible liquids	,,	n-Butanol	0.2958	2.80	0.2007	1.74	26.3
10.		,,	Iso-Butanol	0.3197	3.80	0.2019	1.75	20.8
11.		,,	tert-Butanol	0.2765	5.80	0.1621	1.41	14.7
12.		,,	Methyl Ethyl Ketone	0.1952	0.41	0.3356	2.91	70.9
13.	Immiscible liquids	,,	MIBK	0.2291	0.59	0.3087	2.68	62.9
14.		,,	Xylene	0.1555	0.63	0.2011	1.75	61.4
15.		,,	Cyclohexane	0.1798	0.90	0.1898	1.65	52.4
16.		,,	Iso-Amyl alcohol	0.2765	3.86	0.1740	1.51	20.6

$$\text{*Normalized Absorbance} = \text{Absorbance} \times \frac{\text{Viscosity of water} + \text{Viscosity of organic liquid}}{2 \times \text{Viscosity of organic liquid}}$$

$$\text{**Enhancement} = \frac{\text{Normalized Absorbance (organic medium)}}{\text{Normalized Absorbance (aqueous medium)}}$$

sample and different organic liquids will have different flow-rates (through a single capillary). In case of analysis of oils, particularly lubricating oils, the standards and samples should be preferably matched in viscosity. In case of DCS, the flow rate of the samples is same for both lower ends when solutions of same viscosities are aspirated simultaneously. When an aqueous sample is aspirated through one end and organic liquid through the other, the flow rates of the aqueous sample and organic liquid will be different due to their dissimilar viscosities.

The flow rates of the aqueous sample and the organic liquid, aspirated through the two lower ends simultaneously, were measured. The flow-rate of the sample through one end was found proportional to the viscosity of liquid fed through the other. If the nebulizing pressure is kept constant, by aspirating the organic liquid and aqueous sample through separate ends, the flow of the latter is less than that of the former, when viscosity of the former is less than that of water and *vice versa*.

Since the flow of the sample has direct relationship with absorbance, the effect was studied with aqueous, methanolic and ethanolic media. Methanol and ethanol were selected for the purpose of this study because they are completely miscible with water and the viscosity of water lies in-between those of methanol and ethanol. The copper standards in aqueous, methanolic and ethanolic media with different combinations have been used for this study (Table 2). As these alcohols are completely miscible with water the water-alcohol mixture at the junction of DCS is homogeneous and their percentages do not change for the blanks or the copper solutions for the same system. Only the copper concentration at the junction varies with the flow rate of the particular medium, which is responsible for the change in absorption. The ratio of the absorbances (of a and b in Table 2) is exactly the ratio of the viscosities of the media. This clearly suggests that viscosity correction can be applied to the absorbances. However, the flow-rate correction can also be applied. In this study viscosity correction has been preferred as it is simpler.

(b) *Immiscible Liquids*: At the junction of DCS, the composition of miscible liquid and water is homogeneous and the copper salt is soluble in both the media. The viscosity correction on the absorption and the enhancement is quite understandable. In the case of immiscible organic liquid, the effect was studied on a copper solution (4 μg/ml). Copper was chelated with APDC and extracted into 10 ml MIBK. Aqueous copper standard (4 μg/ml) was aspirated through one end of the capillary and the MIBK blank—which is immiscible—through the other. Similarly 4 μg/ml copper in MIBK was aspirated through one end and water through the other. It was found that the change in absorbance is due to the difference in viscosity (Table 2). Since the copper-APDC chelate is formed in aqueous phase and extracted in MIBK, this is merely a transfer of the chelate from water to MIBK phase. Though MIBK is immiscible with water, copper APDC chelate could be uniformly distributed in the mist like copper in the aqueous phase. It may not be correct to infer from the above observation that the aqueous-MIBK system acts through the DCS like miscible ones. For further verification, NBS organo-metallic compound of iron was taken in MIBK. Both iron com-

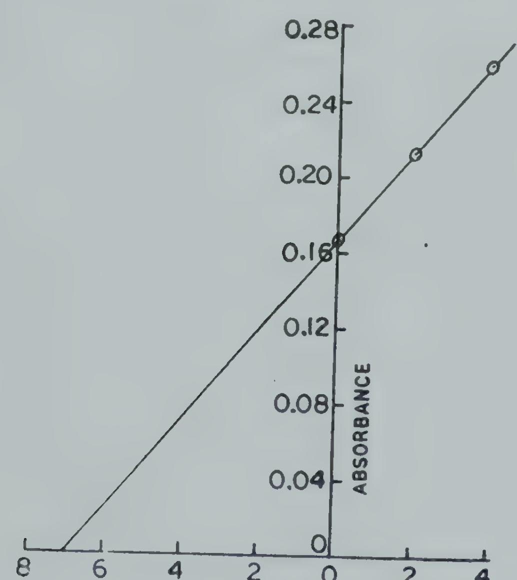
TABLE 2—Viscosity Study of 4 μg./ml. of Copper in Water and Organic Media

Type of Solvent	Sl. No.		DCS (1:1)		Absorbance	Absorbance Ratio of a to b	Relative Viscosity at Room Temperature
			Left arm	Right arm			
Water-Miscible Solvent	1	a	Cu (aqueous)	MeOH	0.1561	0.59	0.59
		b	Water	Cu (MeOH)	0.2612		
	2	a	Cu (Aqueous)	EtOH	0.1986	1.68	1.69
		b	Water	Cu (EtOH)	0.1180		
	3	a	Cu (MeOH)	EtOH	0.4547	2.85	2.86
		b	MeOH	Cu (EtOH)	0.1597		
Water-Immiscible Solvent	1	a	Cu (aqueous)	MIBK	0.1549	0.60	0.59
		b	Water	Cu (MIBK)	0.2565		
	2	a	Fe* (aqueous)	MIBK	0.1002	0.60	0.59
		b	Water	Fe* (MIBK)	0.1662		

*4 μg./ml. of iron

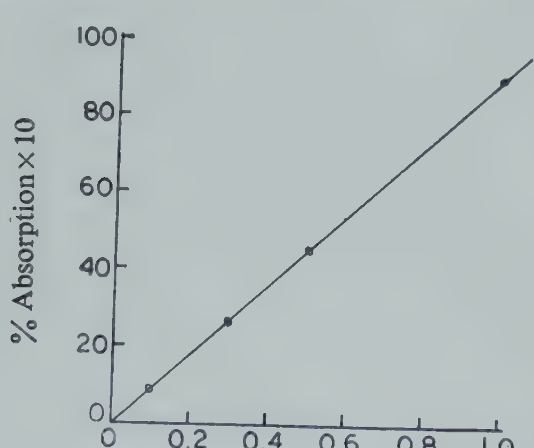
pound and MIBK are immiscible in water. Firstly, 4 μg/ml of iron in MIBK and water blank and then 4 μg/ml aqueous iron standard and MIBK blank were aspirated as above. It is seen (Table 2) that the ratio of absorbance of (a) to (b) is equal to the viscosity of MIBK. The standard addition method was also employed[2] to estimate iron in MIBK by aspirating aqueous standards in conjunction with 4 μg/ml of iron in MIBK medium through separate ends (Fig. 1). The value obtained after viscosity correction is 4.13 μg/ml. These observations suggest that aqueous standards can be employed with DCS for estimating the impurities in immiscible organic liquids.

Trent[4] has observed that tetra-methyl lead and tetra-ethyl lead give different absorption for the same amount of lead and the absorption is different for different solvents. This may be the case for a highly volatile compound of lead, but it appears that for practical purposes the aqueous standards can be used for medium and low volatile elements with DCS, after applying the viscosity correction.



Fe Added, ppm

Fig. 1—Standard Addition Curve for Estimation of Iron in MIBK with Aqueous Addition Standards Using DCS (1: 1).



Fe, ppm

Fig. 2—Calibration Curve for Iron Obtained by Aspirating Aqueous Standards and Blank Simultaneously Through the Lower Ends of DCS (1: 1).

(3) *Estimation of Iron in Naphtha*: The naphtha samples were diluted in the ratio of 1:5 with MIBK. Since the content of iron in naphtha is very low, it has been estimated with the help of a recorder. The calibration curve (Fig. 2) is obtained by aspirating aqueous standards and MIBK simultaneously through separate ends. Similarly, naphtha samples and water were aspirated through the two ends of the DCS. The viscosity was determined and its correction applied (Table 3). The correction can also be applied directly for drawing the calibration curve.

TABLE 3—CONCENTRATION OF IRON IN NAPHTHA SAMPLES, μg./ml.

Sample No.	Iron in Working Sample, μg/ml C	Iron in Naphtha, μg/ml. (C × 5) C′	Iron in Naphtha after Viscosity Correction, μg/ml. (C′ × 0.59)
1.	0.30	1.50	0.89
2.	0.37	1.85	1.09
3.	0.33	1.65	0.97
4.	0.38	1.90	1.12
5.	0.40	2.00	1.18
6.	0.38	1.90	1.12
7.	0.35	1.75	1.03

Conclusion

Aspiration of the samples, when fed simultaneously through the separate ends of DCS, varies inversely to the viscosity of the samples. When the immiscible solvent-aqueous system is used with DCS, the behaviour in the flame is similar to the miscible solvent-aqueous system. This suggests that aqueous standards can be used for estimation of impurities in water-immiscible liquids, such as petroleum products, after applying correction for viscosity. Iron has been estimated in naphtha samples using aqueous standards.

Since the viscosity is affecting the flow rate, which in turn changes the absorption, the viscocity of the mixture can be determined by AAS, if a known amount of an analyzable element is present in the sample.

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[Original mss. received on May 14, 1971]

Diffusion of chlorine ions through films of three different commonly used synthetic enamel paints has been discussed and compared by radio-tracer technique utilizing the long-lived β emitter Cl^{36}.

Diffusion of Chlorine Ion by Radio-Tracer Technique

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Introduction

The importance of ionic diffusion through paint films and other protective coatings is well established[1,2]. Such coatings normally behave like membranes. The ability to combat corrosion depends mainly on their resistance to the diffusion of moisture and other corrosive elements. However, the degree of corrosion protection is also guided by other factors, like osmosis, endosmosis, air permeability, etc., through such membranes[3,4]. In particular, whenever a paint or a protective coating is used to prevent corrosion on a metal surface in contact with a liquid medium, its electrolytic resistance is considered to be much more important than its resistance to water-permeability. Because, a flow of ions through the protective film forming an electrolytic current is then essential for the completion of corrosion cycle. The electrolytic resistance of a paint or a coating is directly related to its capacity for impeding diffusion of ions present in the electrolyte. This property will, therefore, be different for different paints and coating materials.

The purpose of the present investigation is to study the various aspects of ionic diffusion of different corrosive elements through the films of some commonly used paints and protective materials. Here results have been reported for the diffusion of chlorine ions through the film of three synthetic enamel paints (black) of different make utilizing radio-tracer technique with long-lived β-emitter Cl^{36} in hydrochloric acid.

Experimental

The basic part of the experimental set-up consists of a perspex diffusion cell (Fig. 1), having two compartments, C_1 and C_2, each of 60 ml inner volume. They are partitioned by the film of paint to be investigated and then fixed together in such a manner that each compartment becomes watertight except for the diffusion through film.

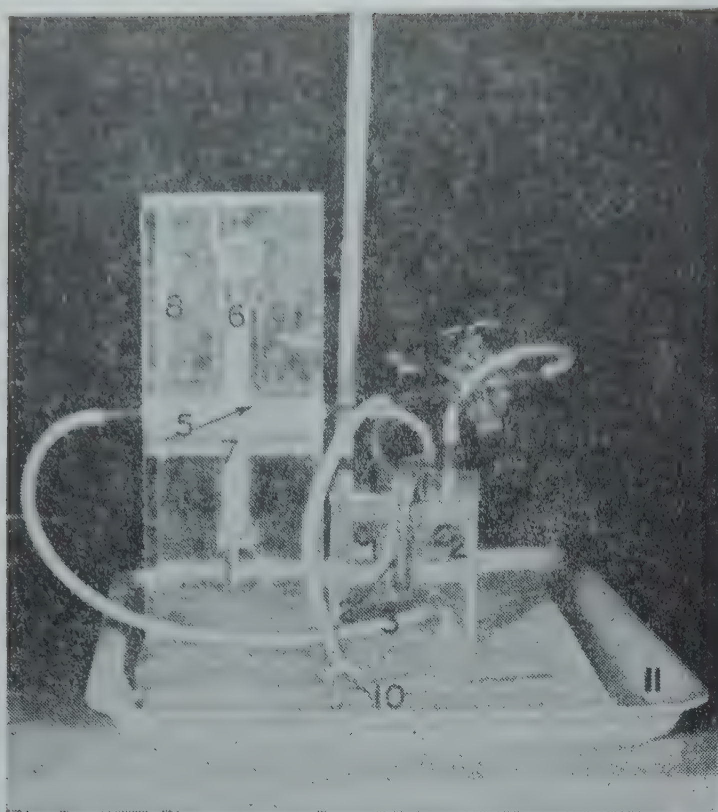

Fig.1—Diffusion Cell

1. Diffusion Cell (C_1—Compartment filled with Radioactive Solution C_2—Initially Filled with Distilled Water).
2. Film of Paint Separating C_1 and C_2
3. Outlet for C_2
4. Inlet for C_2
5. Cavity (embedded inside the perspex mount-8).
6 & 7. G. M. Tubes
8. Perspex Mount
9. 3-way Stopcock
10. Glass Syringe
11. Stainless Steel Tray

The circular portion of the rectangular film allowing diffusion has a surface area of 12.57 sq. cm. Compartment C_1 of the cell is kept filled with a radioactive solution of hydrochloric acid tagged with Cl^{36} of Sp. activity 900 μci/g. chlorine, while distilled water is poured into the other compartment, C_2. The concentration of chlorine ions is always maintained at 10.28 μg./ml. of the radioactive hydrochloric acid. The liquid levels in C_1 and C_2 are maintained same which also cover the entire effective surface of the film. Compartment C_2 will, therefore, accommodate the diffused chlorine ions from C_1. Its outlet is then connected to the β-counting assembly which includes two organic quenched end-window G. M. tubes with their mica windows (thickness: 1.5 mg/cm²) facing each other across a narrow mica-covered cavity of diameter 2.54 cm. and depth 0.5 cm. embedded in a perspex mount, which also holds the G.M. tubes. The liquid from C_2 is sucked in this cavity for assessing β-activity. Before each measurement, the liquid is sucked and recirculated several times in C_2 by means of a glass syringe connected through a three-way stopcock to ensure proper mixing of liquid and also for the complete removal of air from the cavity. The two G. M. tubes are kept at anticoincidence for minimizing the background activity and connected to the electronic scaling system (not shown in the figure). The films are made of thickness 2 mg./cm² by spreading the paint uniformly on the emulsion side of photographic paper according to the free-flowing method. These are then kept in the vertical position, air-dried for a week and finally stripped off the photographic paper by dipping in distilled water for about 15 min. Diffusion through each film is studied at 27°C for about one and a half months at close intervals.

Results and Discussion

The amounts of chlorine ions diffused through the unit film area of three different paints, a, b and c, for a period of about 50 days are shown in Fig. 2. Fig. 3 shows

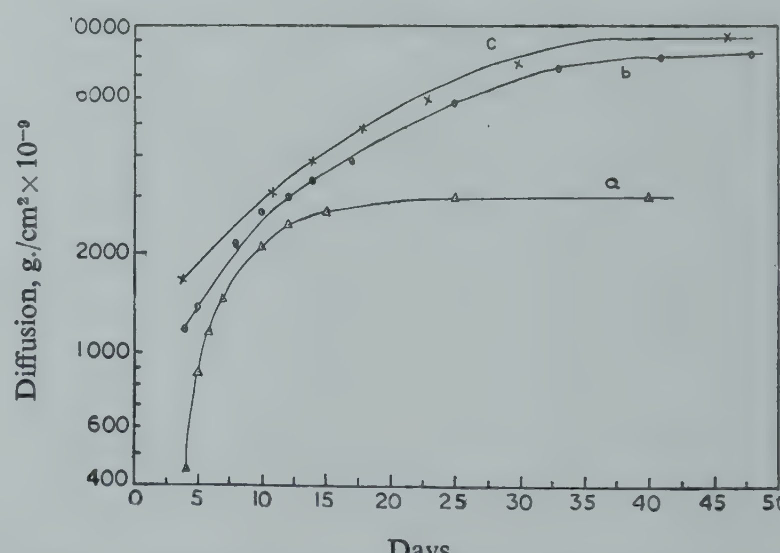

Fig. 2—Diffusion vs Time for Chlorine Ion Through Unit Film Area of Three Different Paints (Film Thickness: 2 mg/cm²)

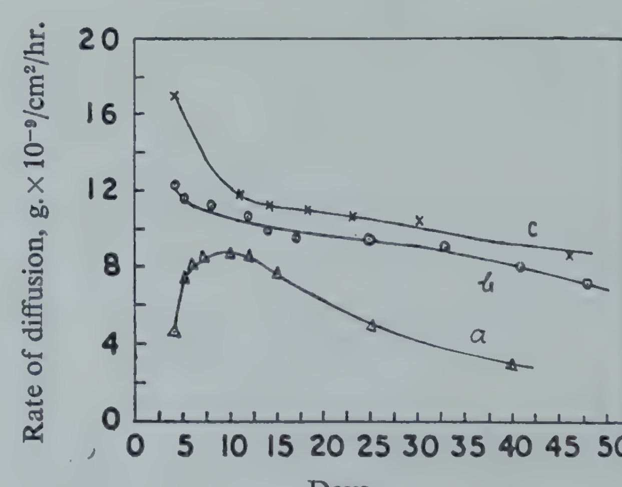

Fig. 3—Rate of Diffusion vs Time for Chlorine Ion Through Unit Film Area of Three Paints. (Film Thickness: 2 mg./cm²)

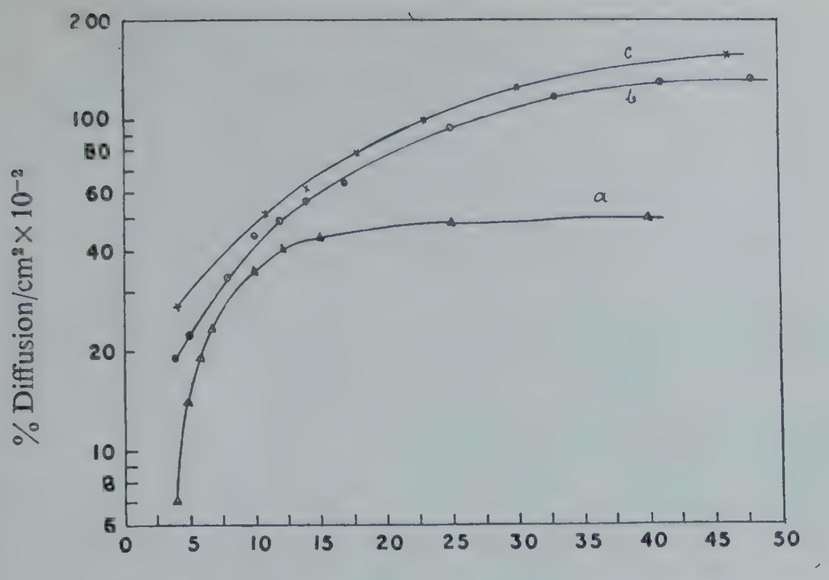

Fig. 4—Percentage of Diffusion vs Time for Chlorine Ion Through Unit Film Area of Three Paints. (Film Thickness: 2 mg/cm²)

the corresponding rate of diffusion/unit area/hr, while the percentage of diffusion/unit area is shown in Fig. 4. The graphs predict that the diffusion of chlorine ions through films of paints a, b and c obeys Fick's laws whose simplified applicable form may be stated as[5]

$$q = \frac{D.A.t.}{X}$$

where q = quantity diffusing in time t
D = diffusion coefficient
A = area of cross-section of the film
X = thickness of the film.

From Fig. 2 it is clear that the paint 'a' allows the minimum and paint 'c' the maximum permeation of chlorine ions under identical conditions. The nature of b is, of course, in-between that of 'a' and 'c'. The diffusion through 'a' tends to acquire a saturation value after a period (T) of 30 days, whereas T is about 45 days for 'b' and 'c'. The $T\frac{1}{2}$ values of 'a', 'b' and 'c' are found from Fig. 2 to be 7.5, 17 and 16.5 days respectively. Fig. 4 gives the percentages of chlorine ions diffused through the paints a, b and c which at time T are 0.48, 1.30 and 1.54 per cent respectively of the initial concentration. The rate of diffusion, however, shows a slow and uniform fall in each case after an initial period of non-uniformity (Fig. 3). It may be concluded, therefore, that amongst the three paints investigated, 'a' is the best so far as the prevention of chlorine ion diffusion through it is concerned. The process may also be utilized for the diffusion studies of several other corrosive elements.

Acknowledgements

The authors are thankful to Sri K. C. Banerji, Dy. Supdt. Physical Research Wing, for his interest in the work. Their thanks are also due to their colleagues, Sri R. Choudhury for taking photograph of the diffusion cell and Sri K. N. Pal* for his assistance in setting up the electronic scaling system.

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[Original mss. received on May 22, 1971]

This note is a preliminary description of small scale penecontemporaneous and deformational structures observed in Krol sediments around Nainital. From the large polished sections, cut normal to bedding, the structures were studied.

Sedimentary and Deformational Structures of the Krol Formation in and around Nainital Area, U.P.

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The presence of these structures should be of significance when it is remembered that the large-scale tectonic inversions are frequent in the rocks of this region.

The chief constituent rocks of this area are (a) green shales, (b) variegated shales with dolomitic alternation, (c) dark grey dolomite limestone and the brown limestone alternating with (d) shales. Units a and b correspond to the Infra Krol while units c and d correspond respectively to the Lower and Upper Krols. The previous studies, done around Nainital region by Auden[1], Heim and Gansser[2], suggest a *Permo-triassic* age to these rocks and a basinal deposition for them.

Infra Krols occupy the centre, northern and eastern flanks of the lake while the western flank is made up dominantly of Krol limestone. The Krols consist mostly of dark grey coloured fine grained occasionally dolomitized limestone showing typical elephant skin alteration and frequently alternating with calcareous shales, which have been transformed into the pencil slates due to the development of a strongly selective cleavage. Frequently intercalated cherty limestone has been encountered in the present area which shows well preserved sedimentary structures, like current bedding, ripple marks, etc. These structures, however, can be classified broadly into primary and deformational types. A typical phosphoria horizon has been found to occur in the Krols of Nainital area[3]. In thin section, the entire rock shows a framework of constituents which have been completely recrystallized resulting in the complete destruction of the original texture.

Primary Structures

Ripple marks, flute casts, cross-bedding and prod marks are the important primary structures observed in the present area.

Ripple Marks: Both simple as well as interference ripple marks (Figs. 1 and 2) have been found. In the simple type, which is symmetrical, the ripple crest is straight and continuous while in the asymmetrical types it is wavy and continuous. The interference of the ripples resulted in the formation of polygonal pits. The wavelength varies from 0.7 to 1.00 cm. Because of fewer number of occurrences, the parameters of ripple characteristics were not studied in a detailed manner.

Flute Casts: The flute casts are deformed in nature (Fig. 3). These specimens were cut perpendicular to bedding indicating this nature. The length of the flutes varied from 6 to 8 cm. while the breadth ranged from 2 to 4 cm. The individual flutes, which showed smooth outline, are either lingui-form or bulbous in nature. The infilling is cross-laminated in nature. Smaller deformed flutes are found to occur in-between the two larger flutes, which are arranged in parallel rows; in plane they show a definite preferred symmetry.

Cross-Bedding: Cross-bedding (Fig. 4) occurring in these rocks is of a smaller scale and unit, and can be called ripple cross-lamination, which according to Jopling and Walker[4] is a genetic term applied only to cross-stratified deposits in which ripple topography is seen. The ripple drift cross-lamination is applied to cross-stratified deposits in which a definite ripple topography is associated with the climbing of one ripple up the stoss side of the ripple immediately downstream[5,6]. In Figs. 1 and 2, a gradation sequence of forms from climbing sets of lee-side laminae (Type 1 of Walker[6]) to ripple

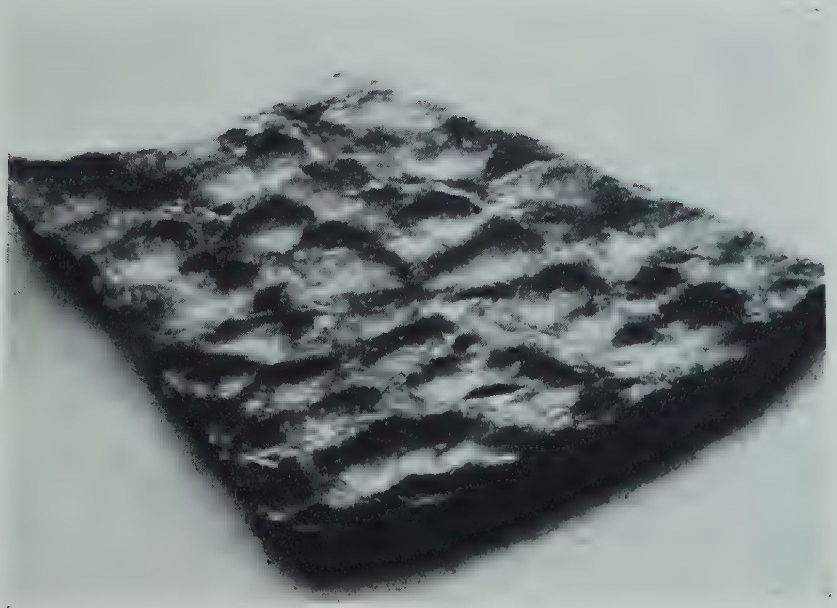

Fig. 1

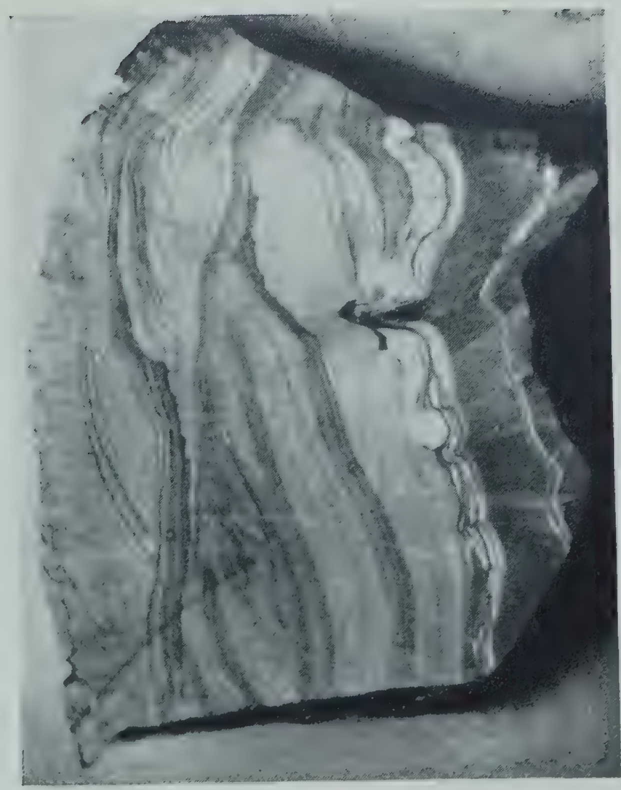

Fig. 4

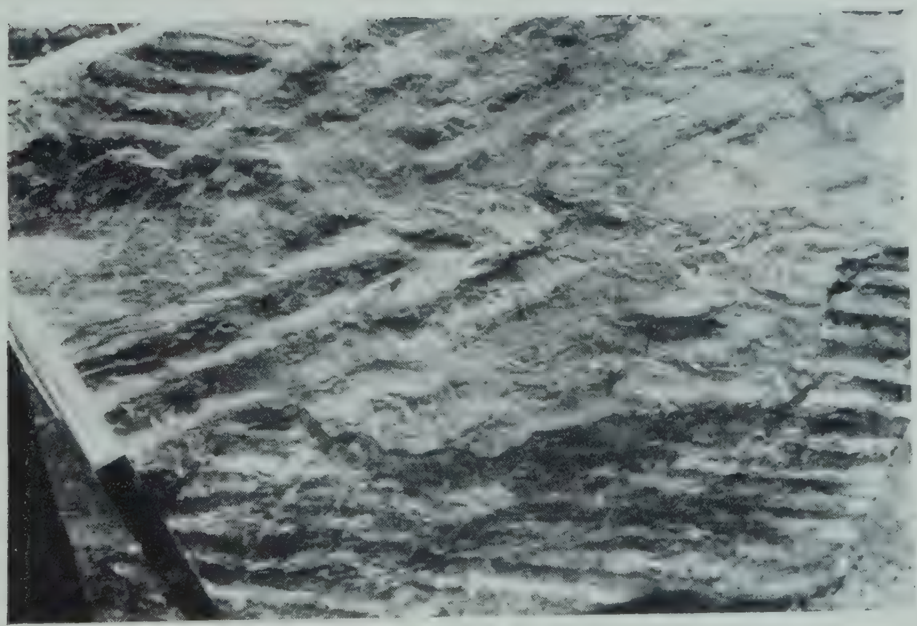

Fig. 2

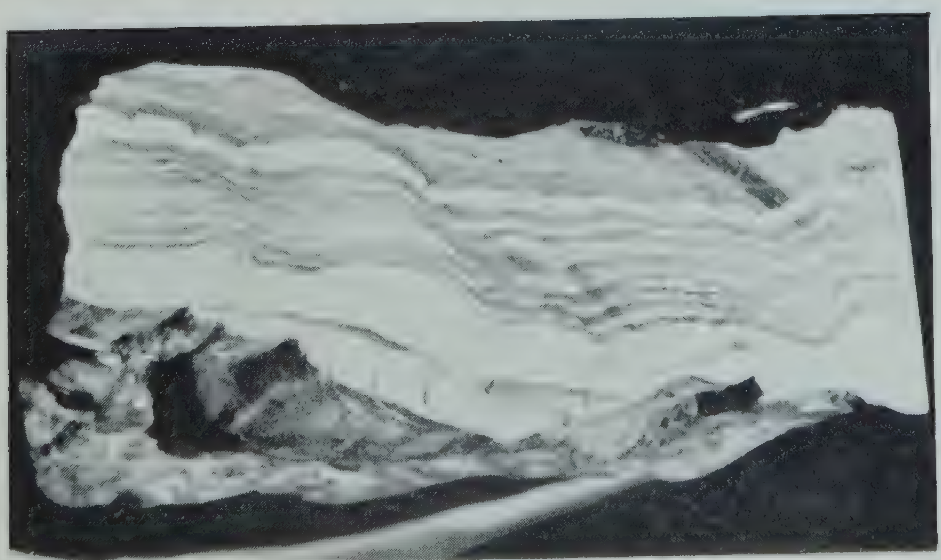

Fig. 3

Fig. 5

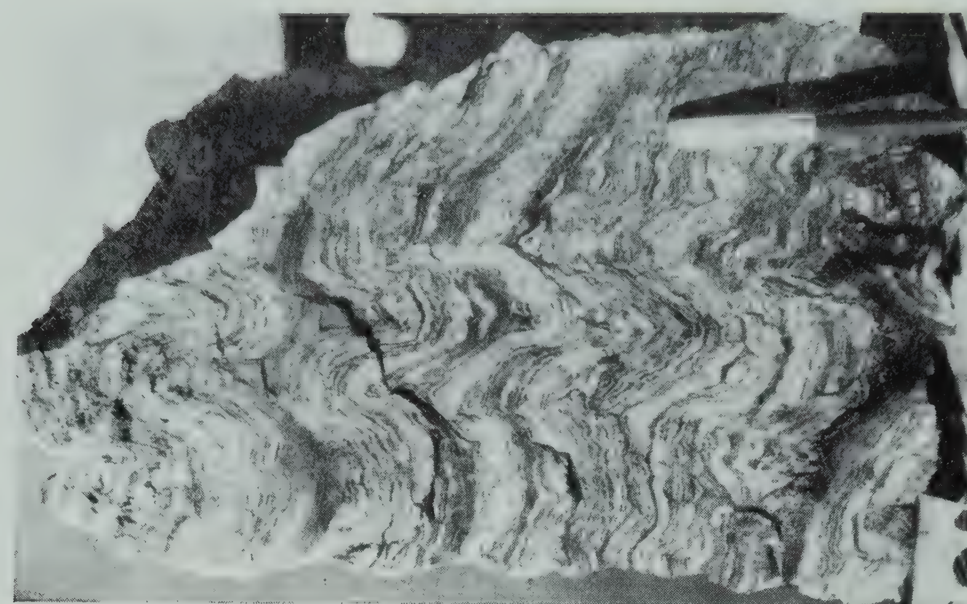

Fig. 6

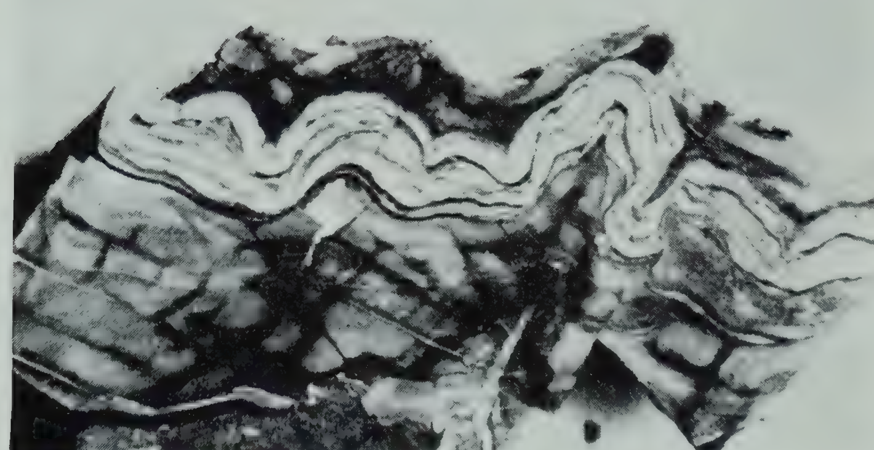

Fig. 7

drift cross-laminae with the intermediate sinusoidal ripple laminae can be observed.

Sorby[5] was probably the first to notice the small scale cross-bedding as the product of ripple migration[7]. On the basis of a review of several studies on modern environments McKee[8], using flume studies, revealed that most of the small scale cross-bedding were the product of ripple migration during flow in the lower part of the lower flow regime[9]. According to Jopling and Walker[4] the main factor controlling the changing type is the ratio of suspended to traction load. The ripple cross-lamination represents a dominant bed-load movement, while sinusoidal ripple laminae represents a fall-out from suspension. The ripple drift cross lamination forms a gradation between the two types.

Prod Marks: In the bedding planes, elongated asymmetrical semiconical depressions are observed. The ribs are having sharp margin with the adjacent deep furrows. The structures are termed as Prod marks[10] (Fig. 5). In one end, the ribs are converging while in the other they are diverging in the form of a comma. These marks must have formed by the tools carried by the current, which may be shale fragments.

Deformational Structures

Minor folds are developed in the chert hard black interlaminated limestone. In Fig. 6 the structure represents a flexure slip-fold with the following conspicuous features: the reversal of closure, caspate nature at the core of the fold and progressive broadening of the folds away from the core, sympathetic offset and the general tendency to maintain constancy of orthogonal thickness.

Fig. 7 represents essentially an asymmetrical and disharmonic fold with considerable amount of flowage. The evidence of interference of the fold axes are also observed.

The deformational structures may be due to post tectonic slumping and mass gliding or gravity gliding as explained by Thomas[11] for the formation of lakes. The sedimentary structures definitely throw some light on the depositional environments of these sediments. The sediments have been deposited in calm and quiet water with moderate wave action resulting in the formation of these primary structures, which can be used to determine the top and bottom of the various beds of this region.

Acknowledgement

The authors' thanks are due to Sri K. C. Banerji, Deputy Superintendent, Physical Research Wing, P and D Division, for encouragement and help during the course of the field and laboratory studies.

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Oxidation of N bis (β-aminoethyl) dithiocarbamic acid has been effected by treating an aliquot of the sample with an excess of the potassium ferricyanide solution in a 7 per cent potassium hydroxide medium. The excess of the ferricyanide is then back titrated with a standard arsenious oxide solution amperometrically.

Oxidation of N-bis (*Beta*-Aminoethyl) Dithiocarbamic Acid with Alkaline Ferricyanide

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Potassium ferricyanide has been used for the oxidimetric determination of many organic as well as inorganic substances in neutral or alkaline media[1]. It belongs to the group of oxidants in which the active species is a complex abstracting ion, $Fe(CN)_6^{3-}+e$ $Fe(CN)_6^{4-}$. Although the oxidation potential of the couple in an alkaline medium is only -0.4 to 0.5 V vs N.H.E[2], it acts as a powerful oxidizing agent by virtue of the reduced oxidation potential of the system containing the reductants in alkaline medium. The reaction could be catalysed by osmium tetroxide[3] or promoted by the addition of zinc (through the formation of insoluble zinc potassium ferricyanide, $K_2Zn_3[Fe(CN)_6]_2$.

Oxidation by potassium ferricyanide offers many advantages, such as high purity of primary standard grade[4], high equivalent weight, extreme stability and applicability in alkaline medium, etc. Like a great majority of oxidants, ferricyanide may be used for direct titration or added in excess and back-titrated. Earlier observations reported the oxidation of thiourea and thiocyante by alkaline ferricyanide[5-6]. Solymosi and Varga[7] determined 4 to 18 mg. of sodium sulphide with this reagent.

$$S^{2-}+8\,Fe(CN)_6^{3-}+8\,OH^- = SO_4^{2-}+8\,Fe(CN)_6^{4-}+4H_2O.$$

In the present study, N-bis — (β-aminoethyl) dithiocarbamic acid has been oxidized quantitatively by the addition of excess ferricyanide and a few drops of osmium tetroxide as a catalyst. The excess ferricyanide was then back-titrated with a standard arsenite solution[7] and the end-point detected amperometrically.

Experimental

Reagents: Potassium ferricyanide solution was prepared from a pure B.D.H. AnalaR quality sample. It was further standardized by the procedure described by Deshmukh *et al*[8]. Sodium arsenite solution was prepared from an E. Merck sample and standardized against bromate. The preparation and standardization of N-bis (β-aminoethyl) dithiocarbamic acid have been described earlier[9-10].

Apparatus: A compact manual amperometric unit[11], complete with a potentiometer and a suitable spot reflecting galvanometer as a current-measuring device, was used for carrying out these titrations.

Procedure: An aliquot of the reagent solution was taken and its alkali concentration was maintained at 7 per cent. A known excess of ferricyanide and two drops of osmium tetroxide were added and the contents were kept aside for 15 min. to ensure complete oxidation. Excess ferricyanide was then back-titrated with a standard arsenite solution. The end-point was detected amperometrically. At an applied potential of + 0.1V vs SCE, the cathodic current of ferricyanide decreased upto the end-point and then remained steady with execss ferricyanide. The volume of arsenite required for unreacted ferricyanide was determined graphically. A blank titration was run simultaneously. From these observations, the amount of ferricyanide consumed during the oxidation and the molar equivalent of oxidant required per mole of the reagent was calculated. The results of a set of experiments with different amounts of the reagent is presented in Table 1.

TABLE 1—OXIDATION OF N-BIS (β-AMINOETHYL) DITHIOCARBAMIC ACID BY FERRICYANIDE

[N-bis (β-aminoethyl) Dithiocarbamic Acid Conc $=1\times10^{-2}$M Potassium Ferricyanide Concn. $= 5\times10^{-2}$M, Overall Alkali Concn. = 7 per cent]

$C_5H_{13}N_3S_2$ Taken, ml.	Ferricyanide Consumed, ml.	Number of Equivalents of Oxidant Consumed per mole of $C_5H_{13}N_3S_2$
0.5	1.59	15.90
0.6	1.92	16.00
0.8	2.58	16.12
1.0	3.20	16.00
2.0	6.42	16.05

Results and Discussion

The results (Table 1) show that 16 equivalents of ferricyanide are required for 1 mole of the reagent. Since the reduction of ferricyanide involves only one electron, the mechanism of the total process may be represented as follows: The two half reactions involved are

$$(1)\quad (C_2H_4NH_2)_2\,N\text{-}\underset{\underset{\displaystyle S}{\|}}{C}\text{-}SH + 20\,OH \rightarrow$$

$$(C_2H_4NH_2)_2N\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}OH + 2SO_4^{2-} + 10H_2O + 16e, \ \&$$

$$(2)\quad 16\,Fe(CN)_6^{3-} + 16e\ 16 \rightarrow Fe(CN)_6^{4-}$$

Combining equations 1 and 2

$$(C_2H_4NH_2)_2\,N\text{-}\underset{\underset{\displaystyle S}{\|}}{C}\text{-}SH + 16\,K_3Fe\,(CN)_6 + 20\,KOH \rightarrow$$

$$(C_2H_4NH_2)_2\,N\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}OH + 2K_2SO_4 + 16\,K_4Fe(CN)_6 + 10H_2O$$

This mechanism is in accord with that proposed for the oxidation of thiourea[5] and thiocyanate[6]. Studies on the estimation of micro quantities of selenium^{4+} and tellurium^{4+} and their separation with this reagent are in progress.

Acknowledgement

The author's thanks are due to Dr. B. K. Banerjee, Superintendent, Physical Research Wing, for his constant encouragement and for providing necessary facilities.

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A dilatometer has been designed for studying the expansion characteristics of different refractory linings and thermal insulating materials upto 1000°C. The sample probe has been modified for accommodating specimens of small dimension and obtaining accurate values with a dial gauge. The equipment has been utilized for the determination of linear expansion of different specimens. The results are in good agreement with their known values.

A Modified High Temperature Dilatometer for Studying the Expansion Characteristics of Refractory Linings and Thermal Insulating Materials

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Introduction

Thermal expansion characteristics of different materials are very much useful for varied types of design work. In the fabrication of high temperature furnaces and heat-exchangers with refractory bricks, the design variables are primarily controlled by these expansion data. In the field of thermal insulation, particularly of the rigid type, the expansion characteristics are definitely of great importance when these will be utilized for specific purposes. A number of methods[1–3] have been employed to determine the coeffecient of thermal expansion of materials upto high temperatures. The instrumental design differs[1–7] primarily due to the fact that they are very much dependent on the type of the materials to be tested, shape of the samples to be used and the measuring head to record the expansion. Many workers have used the optical means[7,8] for measuring the change in length of the test samples but the direct measurement of the dimensional change during heating using a dial gauge has been recommended by different workers[9]. It has been shown that the latter arrangement is less complex giving comparatively more accurate results than in the former one. Each instrument fabricated till now has its own limitations for a particular type of measurement and therefore attachments are provided to make it multipurpose in use.

In the present study, an attempt has been made to fabricate an instrument for measuring linear changes either expansion or contraction of materials, particularly refractories and thermal insulating materials, from room to moderately high temperature.

Apparatus

The apparatus (Fig. 1) consists mainly of a tube furnace in which Kanthal wire for use as an electrical heating element is wound on a sillimanite tube. Both ends of the furnace are open. It is placed on a small stand along with a sliding mirror arrangement through which the inside can be visualized for arranging the sample in a suitable manner without touching the walls of the fur-

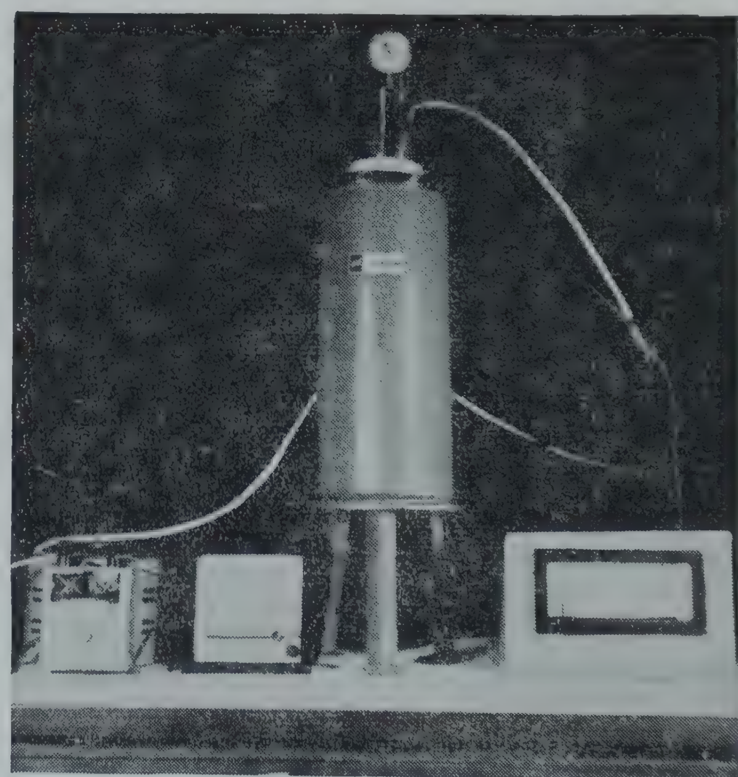

Fig. 1—High Temperature Dilatometer

nace. Its essential part is the sample probe which is a Vitreosil tube having 2 cm. inside diameter with lower end sealed, on which the sample is placed. There is a thin collar at the upper end of the tube, which is fixed on a metallic support to avoid lateral movements. The sample probe is placed on the upper plate of the furnace after inserting the sample. The expansion of the sample is propagated through a quartz rod of about 30 cm. length and 0.7 cm. diameter with a small flange at each end. One flange of the rod is fixed with the sample and the other end is connected with the leg of the dial gauge for recording the expansion. The dial gauge is hinged from a stand in such a way that its leg and the centre of the furnace are in a straight line. The leg is kept at room temperature using a small water jacket so that the temperature effect on the readings of the gauge is avoided completely. The temperature of the furnace, controlled through a variac, is recorded accurately through a chromel-alumel pyrometer. The expansion can be measured at the rate of max. 15°C/min. but here 10°C/min. is the rate which has been selected for all samples. The maximum temperature attainable is 1000°C. A sectional view of the apparatus is shown in Fig. 2.

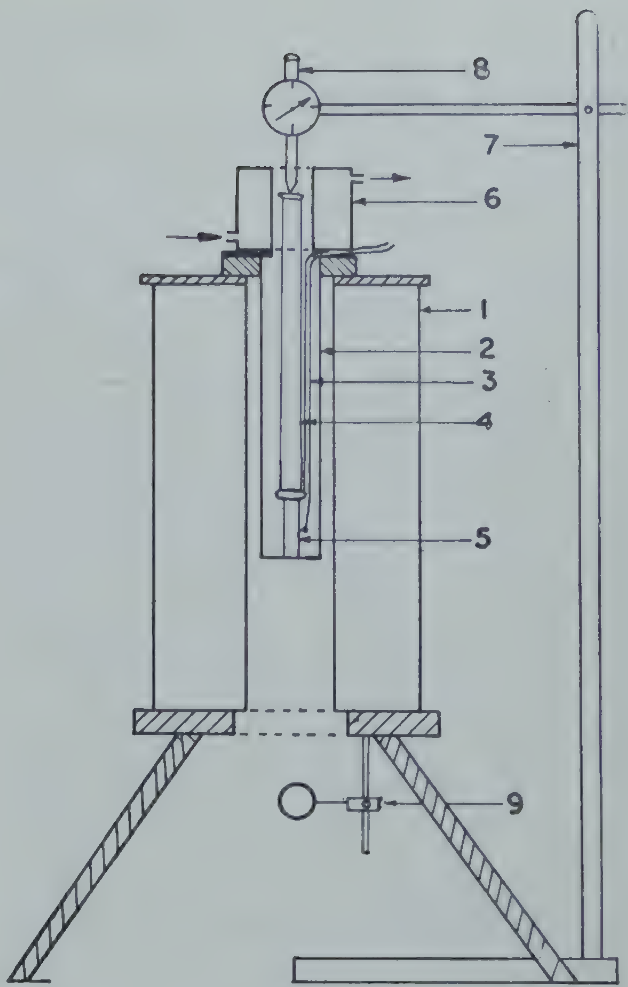

Fig. 2—Sectional View of the Apparatus.

1. Furnace
2. Sample Probe
3. Thermocouple
4. Quartz rod
5. Samples
6. Water-cooler
7. Stand for Keeping Dial Gauge
8. Dial gauge
9. Mirror

Method

The dial reading after the expansion gives the linear compansion of the test sample, which is calculated from the following equation:

$$\alpha = \frac{l_2 - l_1}{l_1 (t_1 - t_2)} \, /°C,$$

where α = coefficient of expansion/°C
$l_2 - l_1$ = linear change, cm.
$t_1 - t_2$ = desired temperature range within which the linear change is measured, °C

There is expansion of the system when it is run without any specimen. For standardization of the apparatus, a run is, therefore, made without any sample following the identical heating rate and other conditions which is to be maintained for measuring the expansion characteristics of the unknown materials. A plot is drawn with temperature against dial gauges reading and the actual linear expansion of the sample, viz. $l_2 - l_1$, is calculated by substracting the dial reading of the system only from that in the case of the sample at a particular temperature. The standardization is usually done before measuring the expansion characteristics of each sample; but it has been observed in this apparatus that variation of the result is not marked at all, even after eight or nine runs with different samples. This is because the sample probe has minimum change upto maximum temperature of the furnace. The specimen sample is made in the form of a solid cylinder having length 5±0.5 cm. and diam. 1 cm. Both ends of the rod are made perfectly smooth for contact between the quartz rod and the bottom plate of the sample probe as well with the leg of the dial gauge. The sample probe has been designed for transmitting the expansion unidirectionally which is recorded in the dial gauge. One minimum division of the gauge is equivalent to a linear change of 10^{-3} cm. Thus with this modification, sample of a small dimension can be used effectively in this apparatus.

Results and Discussion

Standardization of the instrument has been performed with the sample of known expansion characteristics upto 1000°C and with 10°C min. rate of heating. Some refractory bricks are tested for determining their thermal expansion characteristics. The samples are made in the form of small cylinders (5 cm. × 1 cm.) out of full size

bricks by diamond wheel. The variations of their expansion with the temperature are shown in Fig. 3A and the coefficient of expansion has been calculated at a particular temperature range from these graphs. The values obtained for each type of refractory are in good agreement with those reported in the literature (Table 1).

A few low and high temperature thermal insulating materials have also been tested for determining their expansion characteristics (Fig. 3B). Foam glass which is used for the low temperature insulation, expands considerably upto 300°C in comparison to high temperature insulating bricks. The values of the coefficient of expansion of the imported foam glass are in good agreement with the reported values (Table 1). Indigenous foam glass has higher expansion coefficient than that of imported one. The reproductivity of the results was also found to be within ± 1.0 per cent.

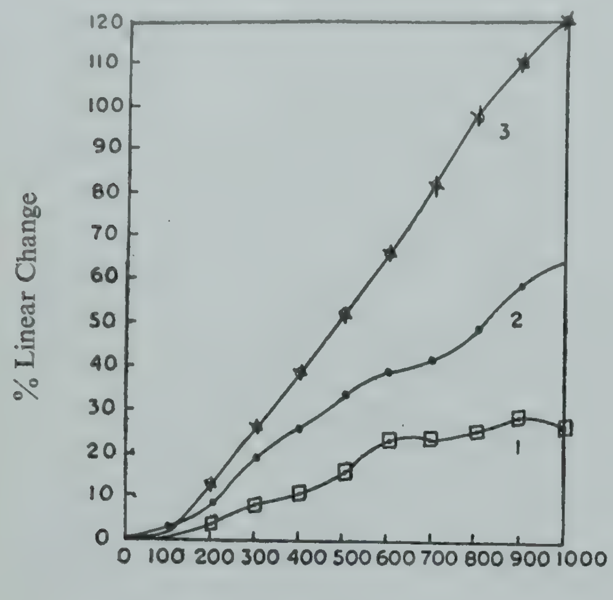

Fig. 3A—Variation of Linear Change with Temperature of Refractories

1. Fire clay 2. Magchrome 3. Magnesite

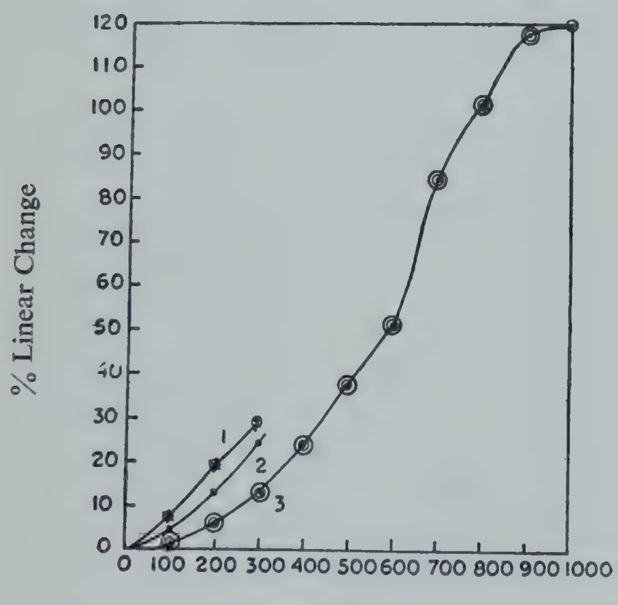

Fig. 3B—Variation of Linear Change with Temperature of Insulating Materials

1. Foam Glass (Indigenous) 2. Foam Glass (Imported) 3. Insulating Bricks

TABLE 1—EXPANSION CHARACTERISTICS OF REFRACTORIES AND THERMAL INSULATING MATERIALS

Sample	Experimental Value/°C Expansion × 10^{-7}	Temp. Range, °C	Reported Values/°C Expansion × 10^{-7}
Fire-Clay	25	300-700	25-30[10]
Magnesite	134	0-1000	130-135[11]
Mag-chrome	64	300-700	65
Foam Glass (Indigenous)	96	0-300	80-90
Foam Glass (Imported)	83	0-300	83
Insulating	152	0-1000	150-155

Acknowledgement

Thanks are due to Dr. B. K. Banerjee, Superintendent, Physical Research Wing, for his keen interest in this work.

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Technical Digest

Use of Indian Rock Phosphate

The rock phosphate deposits, known to exist in Tiruchirapalli in Tamil Nadu, Singhbhum (Bihar), Kasipatnam (A.P.) and in the dyke rocks of Raniganj coalfield (W. Bengal), were so long not commercially exploited because of their (i) low phosphate or high carbonate contents, (ii) scattered nature and other impurities present in them. However, the recent discoveries of intensified and high quality deposits in Udaipur (Rajasthan) and comparatively inferior grade in Jaisalmer (Rajasthan) and Mussoorie (Table 1) have brought in a new era in the phosphate fertilizer industry in India.

Comparative laboratory-scale studies on the reaction and filtration characteristics of the above rock phosphates for the preparation of phosphoric acid by both hemihydrate and dihydrate processes, nitrophosphate sulphate recycle and carbonitric processes and superphosphates have been carried out in this laboratory*.

Reactions with Jhamarkotra Rock Phosphate: This rock is low in carbonate and organic matter, and very little frothing is encountered in its reactions with acids (Table 2). It shows good reactivity in the preparation of superphosphate, which dries up in the course of 3-4 days' curing and sets quickly. However, there is much rise in temperature during acidulation.

Reaction with Singhbhum Rock Phosphate (Mapco's Itagarh Apatite-Quarry): This dark brown apatite (Table 1) has been found to react better in nitric acid reaction for the preparation of nitrophosphate by the sulphate-recycle route. The filterability and washability of the product acid are also good. The gypsum crystals were of thin plate type and the filter cake brown and moist (moisture 40.1 per cent), having P_2O_5 in the cake 0.50 per cent (on dry basis). The product acid on ammoniation showed total nitrogen content 20.0 per cent, P_2O_5 6.0 per cent and pH 5.0.

Nitrophosphate from Singhbhum Apatite by Carbonitric Process: This apatite has the best utilization value in the preparation of citrate-soluble nitrophosphate. No filtration problem is encountered and no beneficiation is required to enrich the P_2O_5 and the reactivity. The

*'Use of Indigenous Rock Phosphate' by M. K. Bardhan, R. U. Singh, A. Ahmad, O. P. Mittal and A. K. Roy.

TABLE 1—ANALYSIS OF DIFFERENT ROCK PHOSPHATE SAMPLES

Component	Rock Phosphate From					
	Jhamarkotra, %	Singhbhum, %		Mussoorie, %	Maton, %	Udaipur-Kanpur, %
		I	II			
SiO_2 + Insoluble	4.87	21.16	24.00	5.03	10.60	4.48
R_2O_3	4.40	—	—	7.54	4.45	1.05
Fe_2O_3	—	14.77	11.25	—	—	—
Al_2O_3	—	2.37	3.47	—	—	—
CaO	47.50	35.86	31.64	44.62	44.90	45.71
P_2O_5	35.63	21.84	24.05	21.21	35.96	15.61
F	3.22	1.50	1.62	2.31	3.80	2.12
SO_3	0.21	—	—	4.89	Nil	0.08
CO_2	1.40	Nil	Nil	10.25	Nil	23.10
Chloride	—	225 ppm	136 ppm	—	300 ppm	100 ppm
MgO	—	Nil	Nil	0.045	Nil	5.83
Loss on ignition	1.40	4.00	3.80	14.51	0.66	25.88

TABLE 2—FILTRATION TIME AND ANALYSES OF GYPSUM CAKES FROM JHAMARKOTRA ROCK PHOSPHATE THROUGH DIFFERENT ROUTES

	Dihydrate Prosces	Hemihydrate Process (Nissan)	Nitrophosphate Route
Rock phosphate (90% passes 100 mesh, B. S.), g.	100	100	100
Filtration Time of Product Acid, sec.	19	22	8
1st washing time with 120 ml water, sec.	10	15	10
2nd washing time with 120 ml water, sec.	10	10	10
Thickness of Cake, mm.	18	18.3	20
Total P_2O_5 in Dry Gypsum, %	0.94	0.28	0.34
Insoluble P_2O_5 Dry Gypsum, %	0.44	0.08	0.18
Water-soluble P_2O_5, %	0.50	0.20	0.16
F, %	0.15	0.067	0.12
SO_3, %	43.12	43.99	43.85
Conversion, %	98.80	> 99	> 99
P_2O_5 in Product Acid, %	29.8 $\left(\frac{w}{w}\right)$	31.21 $\left(\frac{w}{w}\right)$	—
Free SO_3 in Product Acid, %	2.98 $\left(\frac{w}{w}\right)$	2.08 $\left(\frac{w}{w}\right)$	—

analysis of the product is as follows (per cent): Total P_2O_5 13.50, citrate-soluble P_2O_5 13.50, water-soluble P_2O_5 traces, total nitrogen 16.22; pH of 10 per cent solution 6.5-7.0.

Reactions with Mussoorie Rock Phosphate: This rock is quite reactive with sulphuric and nitric acids (Table 3), the assay value of gypsum being more in nitric acid reaction. The gypsum crystals in the sulphate-recycle process were of bigger size than in the dihydrate process. Nitrophosphate prepared by the first process has a low water-soluble P_2O_5. This rock is more responsive for triple superphosphate (having 89.5 per cent soluble P_2O_5) (Table 4), the reaction being found optimum with particular acid concentration irrespective of the initial temperature of the acid. With higher acid concentration (for increasing free acidity in the ultimate product) the mass did not set.

TABLE 3—FILTRATION TIME AND ANALYSIS OF GYPSUM CAKE FROM MUSSOORIE ROCK PHOSPHATE

	Dihydrate Process	Sulphate Recycle
Rock phosphate (90% passing 100 mesh B.S.), g.	100	100
Filtration time of product acid, sec.	15	9
1st washing with 120 ml water, sec.	18	11
2nd washing with 120 ml water, sec.	12	10
Cake Thickness, mm.	20	18
Total P_2O_5 in dry gypsum, %	0.67	0.66
Water-soluble P_2O_5, %	0.22	0.53
Insoluble P_2O_5, %	0.45	0.13
F, %	0.035	0.029
SO_3, %	37.50	42.01
Conversion, %	97.87	>99
P_2O_5 in product acid, %	—	—
Free SO_3, %	—	—

TABLE 4—REACTION CONDITIONS AND ANALYSES OF SUPERPHOSPHATE FROM MUSSOORIE ROCK PHOSPHATE

	Single Superphosphate	Triple Super-Phosphate
Initial acid temperature, °C	50	35
Acid Concentration	76% H_2SO_4	H_3PO_4 of sp.gr. 1.50
Rise in Temperature, °C	46	16
Setting time, min.	30-35	12-15
Cake Character	Sticky mass, swelling was good but setting slow.	Little porous and sticky type, swelling as well as setting were good.
Total P_2O_5, %	17.29	39.23
Water-soluble P_2O_5, %	8.00	35.60
Citrate-soluble P_2O_5, %	0.40	1.63
Citrate-insoluble P_2O_5, %	8.89	2.00
Free Acid, %	0.1 H_2SO_4	2.95 H_3PO_4
pH of 10% solution	3.5	3.2

Reaction with Maton and Udaipur-Kanpur Rock Phosphate: Maton rock, having high P_2O_5 content and no carbonate, did not respond well for the preparation of superphosphate, while the Udaipur-Kanpur sample with low P_2O_5 and high carbonate was considered uneconomical. A mixture of these rocks (Maton: Udaipur-Kanpur as 4:1) having P_2O_5 31-32 per cent gave a single superphosphate which was quite reactive (Table 5). In the second set of values (column 2 Table 5), the initial acid temperature was kept 10°C more than in the first set, but there was no marked variation in the quality of the final product, although there was some improvement in the conversion efficiency and the cake was more porous and cured in a shorter time.

Reaction with Visakhapatnam and Udaipur-Kanpur Rocy Phosphate: Suitable blends of Visakhapatnam and Kanpur rocks have been acidulated for the preparation of superphosphate (Table 6). In a few cases the mass sets quickly after acidulation but in most cases the setting was accelerated by heating the acidulated mass upto 90°C. Only in two cases (b and e, Table 6), the mass set in the usual manner without any further heating after acidulation and the conversion was also comparatively good.

TABLE 5—REACTION CONDITIONS AND ANALYSIS OF SUPERPHOSPHATES FROM MATON AND UDAIPUR-KANPUR ROCK PHOSPHATE MIXTURE

	I	II
Acid Concentration	76% H_2SO_4	76% H_2SO_4
Initial temp. of acid, °C	50	60
Rise in temperature, °C	92	98
Setting time, min.	Within 5	Within 5
Total P_2O_5 in rock phosphate mixture, %	32.67	32.67
Total P_2O_5 in superphosphate, %	21.18	21.18
Water-soluble P_2O_5 in superphosphate, %	19.46	19.54
Citrate-soluble P_2O_5 in superphosphate, %	0.30	0.52
Citrate-insoluble P_2O_5 in superphosphate, %	1.42	1.12
Free H_2SO_4 after 21 days in superphosphate, %	0.22	0.26
Conversion in Superphosphate, %	91.87	92.26
pH of 10% solution Superphosphate, %	3.2	3.1
Retained moisture after 21 days, %	4.97	4.53

TABLE 6—REACTIONS WITH DIFFERENT BLEND RATIOS

Blend Ratio Vizag: Udaipur-Kanpur	Acid Concentration, %	Initial Acid Temperature, °C	Setting time	Total P_2O_5, %	% W.S. P_2O_5	pH of 10% Solution	Conversion, %
(a) 3 : 1	66	70°	Very slow setting	22.22	11.09	3.4	57.68
(b) 3 : 1	66	30°	5 min.	23.09	13.11	3.8	56.78
(c) 2 : 1	70	70°	Slow setting, sets quickly at 90°C on heating	19.20	13.60	2.6	71.57
(d) 2 : 1	65	70°	No setting sets at 90°C on heating	18.94	13.10	2.8	69.15
(e) 2 : 1	66	70°	3 min.	19.13	14.54	2.4	76.02
(f) 2 : 1	66	30°	Slow setting, sets quickly at 90°C on heating	19.0	10.94	2.7	57.50

ERRATA

TECHNOLOGY **8** (1971), No. 1, Jan.-March

	Error	*Correct*
Page 31 Table 2	AISI Type 316	4. AISI Type 316
Page 32 Column 1 Line 1	(Fig. 1, A & B)	(Fig. 1, a, b and c)
Page 32 Column 2 Line 6	(Fig. ID)	(Fig. 1 d)

Reviews

The System of Soil Classification for Canada (Canada Department of Agriculture, Ottawa, 249 pages, 1970)

Soil is a heterogenous system, a systematic classification of which is essential for its identification and management. So, one classification fulfilled all the requirements in the field and from the time of Dokuchaiev and Hilgard till today many systems have been developed in different countries. The emphasis on the systematic classification of Canadian soils was laid in 1940, and with various alterations from time to time a rather stable system has been developed recently.

This monograph comprising seven chapters deals in detail with the survey and classification of Canadian soils. The scheme presented consists of order, great group, sub-group, family, series and type. The exclusion of sub-order is noteworthy. Altogether there are 8 orders, 22 great groups, 138 sub-groups, 800 to 1000 families, about 3000 series and around 4000 types. In one chapter, correlation between the Canadian, American and world systems has been worked out for horizon identification down to sub-group level.

Along with a number of diagrams and coloured photographs, the get-up of the book is attractive. A good deal of knowledge on Canadian soils may be obtained from it.

(B. Chowdhury)

Infrared Spectroscopy—Its Use in the Coatings Industry. By Infrared Spectroscopy Committee of the Chicago Society for Paint Technology (Published by Federation of Societies for Paint Technology, Philadelphia, Pennsylvania 19107, USA. Pages x + 456. Price $30 per copy to non-members).

The very interesting booklet, 'Infrared Spectroscopy—Its Use, as an Analytical Tool in the field of Paints and Coatings', published by the Society in 1961 was as invaluable to the coatings chemist as the present book, which is, in fact, an up-to-date rewriting of the 1961 publication. Undoubtedly, there was a great need of publication for this highly useful book as several changes have occurred during these years.

This new publication contains a compilation of infrared spectra of virtually all materials commonly used in the coatings industry. A sincere effort has been made to include all the newer pigments, solvents, modifiers, additives and vehicles. More definite information of vehicle composition is also given. This would surely prove useful in interpretation of spectra.

The publication also includes a more fundamental and comprehensive treatment of the theory of infrared spectroscopy. Also included are instrumentation, experimental techniques, qualitative and quantitative analysis, selected applications, with the newer sampling techniques, such as specular reflectance, internal reflection, the use of cesium iodide and KRS-5 plates and the triple pressing technique for alkali halide pellets.

This most valuable book contains 740 infrared spectra of materials utilized in the coatings and all other allied areas. A very useful literature survey containing over 500 references is also included.

The reviewer is very much impressed with this comprehensive and up-to-date reference source for infrared spectroscopists and coatings workers. The book is beautifully compiled and printed. It will surely become an invaluable aid to users of infrared spectroscopy in the coatings industry and all other allied areas. The reviewer strongly recommends this interesting publication to infrared spectroscopists, all industrial and government libraries all over India and other countries.

(Vijay Mohan Bhatnagar,
Ontario, Canada)

The Chemistry and Uses of Fire Retardants By J. W. Lyons. (Published by John Wiley & Sons, Inc., New York. Pages xiv & 462. Price $ 22.50).

Fire safety is one of the main concerns of our increasingly safety conscious society. It has been estimated that in the USA about ten thousand people lose their lives every year due to fire, and that annual property loss exceeds $ 1.6 billion. The concern of the legislative bodies and of various authorities entrusted with the improvement of fire safety is increasing throughout the world. Their efforts, of course, will primarily affect future construction. The burden of protecting

such structures falls on fire retardant materials which may be applied over existing surfaces.

Fire retardant coatings contain four basic ingredients causing the phenomena of intumescence to occur and enabling the substrate to resist ignition when subjected to fire: (1) Carbonic—a source of carbon; (2) Catalyst—a source of non-flammable gas; and (4) Binder—a thermoplastic skin.

The mechanism of intumescence consists of the following five steps which make a fire retardant paint work: (1) the catalyst decomposes to form phosphoric acid; (2) the resultant acid reacts with the carbonific; (3) the phosphated carbonific decomposes to form a large volume of foamable carbon and then releases the acid; (4) the resinous material melts to form a film or skin over the carbonaceous material; and (5) the blowing agents release gases which cause the carbon to foam, forming a thick, highly effective insulation.

This highly interesting book covers almost every aspect of fire retardancy. Indeed, this book deals with basic concepts in sufficient detail to provide the layman with an understanding of fire-retardant technology and to provide the specialist with a convenient summary of information in related fields. There are several books now on fire-retardancy but I have found this book up-to-date and covering a good deal of materials. We must accept the fact that a thorough discussion and reference check of all fire retardants would require many volumes. This book contains every essential aspect of the chemistry and uses of chemicals useful for retarding fire in a given system. Besides author and subject indices, the eight chapters include: introduction—an overview; chemistry of fire retardants based on phosphorus; some chemistry of antimony, boron, chlorine, and bromine; cellulose; chemistry, wood, paper and forest fire control; cellulose: textiles; coatings; synthetic polymers with all-carbon backbones; and synthetic polymers with heterogeneous backbones. This interesting publication is strongly recommended for every library throughout India. This book will be valuable to paint, textile (and polymers) manufacturers, to students, teachers; and to all industrial users of these materials.

(Vijay Mohan Bhatnagar,
Ontario, Canada)

Industrial Paint Application By W. H. Tatton and E. W. Dres (Published by Hart Publishing Co. Inc., 510 Avenue of the Americas, New York, Pages viii & 200. Price $ 12.50).

This interesting book describes all established procedures, including brush application, doping, barrelling, flow coating, roller coating, curtain coating, spraying, and silk screen application. A short, elementry section on principles of paint technology has been included so that the reader can appreciate how the composition of various types of industrial finishes is linked with the formation of the final coating.

The comparative merits of several paint processes are discussed, with interesting suggestions as how to overcome faults. The book is written in a very readable style and is not too technical. It has 19 chapters, 12 plates, and an adequate subject index. The chapters include the following topics: Brush and Associated Application, Dip application, Barrelling, Flow Coating, Roller Coating Application, Curtain Coating, Conventional Spray Application, Automatic Spraying, Hot Spray Application, Airless Spray Application, Spray Application of Two-Component Materials, Automatic Electrostatic Spraying, Electrostatic Hand Guns, Silk Screen Application, Some Specialized Applications, Metal Cleaning, Metal Pretreatment, Storing Ovens, and Principles of Paint Technology. Although of direct primary value in finishing shops, it will also prove very useful to industrial technical sales representatives, to students and teachers of paint technology, and to all industrial users of paints.

(Vijay Mohan Bhatnagar,
Ontario, Canada)

Notes & News

Mineral Raw Materials in India for Fertilizers

1. **Rock Phosphate**

Bedded marine phosphorites and veins of apatite are the most important sources of rock phosphate. Other sources are basic clay, coal ash, carbonatite, etc. In Kerala phosphate is also being recovered as a by-product of monazite sand processing. The rocks do not have a definite or fixed chemical composition. The major minerals belong to the apatite group represented by the general formula Ca_5 $(PO_4)_3$ (FClOH), the commonest mineral of this group being apatite, which contains about 42 per cent P_2O_5. The apatite group includes fluor-apatite, chlor-apatite, hydroxy-apatite, francolite, etc. and various other phosphate minerals with a crystal lattice of the apatite type. The vein deposits are composed of coarsely crystalline or granular apatite, while amorphous or massive calcium-phosphate constitutes bedded phosphorites.

The P_2O_5 content can be used to classify phosphorites into the following six quality groups: (1) containing more than 35 per cent P_2O_5 and negligible amounts of admixed material i.e. dolomite, calcite, pyrite, iron oxide and clay (2) containing 28-35 per cent P_2O_5 which can be used in the wet-process making of superphosphate, provided deleterious components are low; (3) containing 18-28 per cent P_2O_5 which could be regarded as suitable for direct application and also for thermal treatment and mething, but benefication is necessary for acid treatment; (4) containing 10-18 per P_2O_5, requiring enrichment before utilization; (5) containing 5-10 per cent P_2O_5 which can be useful provided they are amenable to enrichment and are easily accessible; they can be directly applied in acid soils; (6) containing less than 5 per cent.

Until recently the chief sources in India were the apatite deposits of Andhra Pradesh and Bihar, nodular phosphate beds of Tamilnadu and Guano deposits of Laccadive Aminidive islands. Sizable deposits have been recently located in Rajasthan and U.P. After the discovery of rocks in the Palaeozoic Birmania formation in the Jaisalmer (Rajasthan) by Sheldon in 1966, GSI started continued search, which has resulted in the discovery of sizable deposits of pre Cambrian phosphorite in Udaipur district, at Kanpur, Maton, Dakan Kotra and Karbaria Ka Gurha in March 1967. Later in 1968, larger deposits were discovered in Jhamar Kotra area. The importance of the Udaipur deposits lies in their proximity of the superphosphate plant of Hindusthan Zinc Ltd at Debari. Later extensive exploratory operations were taken by the GSI, NMDC, etc. in Rajasthan & UP from Aug 1967 which have just ended.

Jaisalmer Deposits:

Birmania—Palaezoic phosphorite bed mostly phosphatic limestone 1-3 m. thick is traceable for about 400 m in NNW direction. Reserves estimated at 4.89 mil tonnes with average P_2O_5 content 10.15 per cent. **Fategarh**—1-4 m. thick of cretaceous-Eocene age 88, miles north of Barmer, P_2O_5 not exceeding 5 per cent.

Udaipur Deposits:

Maton—Phosphorite horizon is traceable over a strike length of 3.5 km. with thickness upto 20 m. Principally apatite with minor dahallite and gangue of quartz, it is a medium grade rock with P_2O_5 content 13.8 to 34.2 per cent (average 21 per cent). **Kanpur**—its thickness varying from 4 to 6 m. and the P_2O_5 content from 12 to 14 per cent. **Karbaria Ka Gurha**—the phosphorite has been traced over 1500 m. having thickness 1-5 m. Tentative reserves are 0.56 mil. te. with 22-25 per cent P_2O_5.

Dakan Kotra—a well-marked horizon 6-8 m. thick associated with dolomitic marble extending for about 500 m. and has a P_2O_5 content of about 15 per cent; reserves estimated at 1.4 mil. te. **Jhamar Kotra**—the largest single deposit so far known in India. The phosphorite horizon is exposed over a length of 16 km. with the thickness averaging 15 m. The deposit is divided into 7 blocks (A to G) of which D block extending over 1600 m. strike length is the richest, with 30-37 per cent P_2O_5 usable directly for making superphosphate. Production from D block started in 1969 in opencast mines, with present daily raising 400-500 tonnes utilized by Hindusthan Zinc. Ltd., FCI Trombay, DCM at Kota and Gujarat State Fertilizer Co. etc. Production target by 1977-78 is 10,000 te/day **Neemuch Mata**—The 2-3 m. thick phosphorite zone extends intermittently for about 2000 m. Reserves estimated 1 mil. tonne with 12-20 per cent P_2O_5. The material beneficiated to superphosphate grade. **Badgaon**—This is perhaps an extension of the horizon at Neemuch Mata. Preliminary estimates 1 mil. te with 15-25 per cent P_2O_5. **Sisarma**—deposits estimated 0.7 mil. te of 8.12 per cent P_2O_5.

Mussoorie Syncline:

Reported in 1885 but detailed examination of the nodules and rocks started in 1960 and intensive exploration is now in the final stages. Potential phosphorite-bearing zone is about 120 km. but only 10 blocks ranging from 300 to 6500 metres length containing phosphatic horizons of significant thickness (1-15 m.) located in the following areas: **Maldeota West**—Phosphatic zone extends for about 1350 m. thickness varying 2-5.8 m. analysing 20-25 per cent P_2O_5. Reserves estinated 5.13 m. te with 18.6 per cent P_2O_5 as proved and 1.65 m. te as inferred. **Maldeota East**—Phosphatic horizons traced in 3 block—Mathet, Dubra and Chipaldi—and bands barely exceed 1. m. Reserves have been estimated at 0.26 m. te with 20 per cent P_2O_5 in Mathet, 0.235 m. te with 28 per cent P_2O_5 in Dubra and 1 m. te with 25 per cent in Chipaldi. **Durmala**—Phosphorite traced for about 1600 m. with thickness 3-9 m. having 4.58 mil. te reserves with P_2O_5 27.8 per cent. **Partibba-Chamasari**—The phosphatic horizon has a cumulative length of 3600 m. ranging from 1-3.8 m. thickness with 18-31 per cent P_2O_5 and reserves 2.79 mil. te. **Bhusti - Jamthialgaon - Jalikhal** - Continuous extension of about 7.2 km. split by Bandal river. Within the eastern sector phosphorite 0.46-2.55 m. thick extends for 3000 m. with average 30 per cent P_2O_5 (total reserves 2 m. te).

Besides the above areas rock phosphates occur in (i) **Tamilnadu and Pondicherry**—in

Cretaceous sediments probably apatite with limestone silica, iron oxide and clay in Tiruchirapalli with P_2O_5 content 20.5-26.5 per cent (reserves 0.127 m. te) (ii) **Singhbhum (Bihar)**—apatite belt extends about 60 km. reserves 1.07 mil. te, 15.5 per cent P_2O_5 (iii) **Vishakhapatnam** (A.P.)—veins of almost pure apatite associated with vermiculete and magnetite occur in Kasipatnam (P_2O_5 35 per cent). having about 1.1-2 mil. te of high grade ore (iv) **Assam and Meghalaya**—Occurrences of nodular phosphorites (P_2O_5 16 per cent) have been reported from Kopilli formation in the Jaintia, Khasi and Garu (Siju area) hills, possibly extending into N. Kachar and Miker hills. (v) **Himachal Pradesh**—nodules in the Eocene formations upto 21-25 per cent P_2O_5 with associated limestones occasionally up to 20 per cent.

2. Potash

India has so far no commercially exploitable resources of potash. The existing sources are (1) **Reh**—saline efflorescene earth containing potassium nitrate found in Maharashtra, UP, Punjab and Bihar (2) **Saline Lake**—Sambhar in Rajasthan and in Ladakh. (3) **Gulf of Katch and Cambay-Central**—Central Salt and rarine Chemicals Research Institute, Bhavnagar has erected a 25,000 K_2O/yr pilot plant for extracting potash from Little Rann and Cambay.

[Balasudaram, M. S., *Eastern, Metals Rev.*, **24** (April) (1971), 69]

Patents*

Stabilized Ammonium Nitrate-Calcium Carbonate Fertilizer Compositions

M. L. Brown, A. W. Green, and E. L. Blanton (to Mississippi Chemical Corp).

S. African, 69, 07070, Apr. 24, 1970, U.S. Appl. June 20, 1969; 21 pp.

When known agents for stabilizing NH_4NO_3 against changes in crystal structure are added to molten NH_4NO_3-$CaCO_3$ mixed fertilizer, the prills produced are swollen and soft. In the process claimed, the stabilizer is added to molten NH_4NO_3 before introduction of the $CaCO_3$. Prills made in this way are hard and resistant to thermal shock. Preferred stabilizers are ammonium phosphate, boric acid, and $(NH_4)_2SO_4$, and the preferred amount is that required to give 0.01-0.5% of stabilizer in the final product.

(*Fertilizers Abstracts*, **3** (12) (1970), 281)

Inhibition of Urea Hydrolysis

J. R. Anderson (to Imperial Chemical Industries Ltd.,).

U.S. 3,515,532, June, 2, 1970, Appl. Oct. 23, 1967; 3 pp.

Hydrolysis of urea fertilizers in the soil is inhibited by adding a polyhydric phenol (0.05-5% of the urea wt). Thus, a urea solution containing a small amount of urease was hydrolyzed almost completely in 150 min at 80°; when small amounts of catechol, quinol, or benzoquinones were added, hydrolysis was almost completely repressed under the same conditions. Combinations of quinones and phenols were more effective than either inhibitor alone.

(*ibid.* 282)

Prevention of Nitrogen Oxide Emissions from Fertilizer Manufacture

A. B. Funk and J. C. Moore (to W. R. Grace & Co.).

U.S. 3, 528, 797, Sept. 15, 1970, Appl. Nov. 8, 1967; 5 pp.

In nitrophosphate processes, the off-gases from the acidulation vessel containing N oxides, are contacted with an aqueous solution of urea. The following reaction occurs;:$2HNO_2+NH_2CONH_2 \rightarrow 2N_2+CO_2 + 3H_2O$. The reaction can be carried out by scrubbing the off-gases with aqueous urea solution in a tower or by adding urea to the acidulation mass. Compared with the usual method of passing the gases through a limestone packed scrubber countercurrent to a flow of water, the present method gives virtually 10% removal instead of partial removal of the N oxides.

(*ibid*, **4** (1) (1971), 1)

Nitrification Inhibitor

Harou Toyoda, et al (to Matsui Toatsu Chemicals, Inc.).

U.S., 3, 526, 494, Sept. 1, 1970, Japan Appl. Dec. 6, 1966; 3 pp.

A reaction product of sulfathiazole and formaldehyde is effective in decreasing the rate of conversion of ammonium N to nitrate N in the soil. The product was prepared by dropping 50 ml of 37% formaldehyde into a solution prepared by dissolving 100 g sulfathiazole in 1000 ml of 1 N HCl. a fine crystalline precipitate soon formed. The precipitate was filtered off, washed with water, and dried at 75° yielding 98 g of a yellowish-brown powder. It contained C 42.98, H 3.96, N 14.07, and S 22.12%, corresponding to the formula: $C_{21}H_{22}O_6N_6S_4$. When heated to 265° the material melted and decomposed. The product can be applied to the soil as an aqueous suspension or as a dry powder diluted with an inert carrier such as chalk or gypsum. The concentration in the soil should be 1-150 ppm. It can also be incorporated in fertilizers using at least 0.5%, based on the wt of reduced N in the fertilizer, Data are given on the effect of the product on rates of nitrification under various conditions.

(*ibid*)

Steam Reforming of Carbon Monoxide-Rich Hydrocarbon Feeds

I. N. Banchik, et al (to Lummus Co.).

U.S., 3, 527, 565, Sept. 8, 1970, Appl. June 19, 1967; 5 pp.

The title operation is carried out in a tubular furnace. Feed rich in CO, such as gases from the cracking of ethane, propane, and naphtha, is rapidly preheated to over 1300°F. in the absence of a reforming catalyst. The preheated material is then heated to 1400-1800°F. in the presence of a reforming catalyst to produce an effluent containing H. The preheating is done in a radiant heating section of the furnace by providing the upper portion of the tubes in the radiant section with a plug to increase the mass velocity, thereby increasing the rate of heat transfer. The feed gas and the steam are passed downwardly through the tube. Apparatus is described.

(*ibid*, 1)

Catalyst for Reacting Carbon Monoxide with Steam

Ernst Lorenz, et al (to Badische Anilin & Soda-Fabrik A.-G).

U.S., 3,529,935, Sept. 22, 1970, Appl. Germany Apr. 15, 1967; 4 pp.

Catalyst based on Fe containing activators such as Cr are in general use for the reaction of CO with steam to form H and CO_2 (conversion reaction). This patent describes such a catalyst modified by the presence of oxides of Mg and/or Zn and Al_2O_3. Under reaction conditions the catalyst contains 5-95% Mg-Al-spinel and/or Zn-Al-spinel. This catalyst allows higher space velocities and consequently smaller converters. Carbon monoxide conversions

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of 10,000 m^3 (S.T.P.)/m^3 of catalyst/hr can be obtained at 100 atmosphere pressure. Instead of using higher space velocities it is possible to use lower reaction temperatures. The general range of temperature is 180-550°. The catalyst activity remains practically constant for at least one year.

(*ibid*, 2)

Urea Synthesis

Ivo Mavrovic (to Chemical Construction Corp.).

U.S., 3,527,799, Sept. 8, 1970, Appl. Jan. 20, 1966; 5 pp.

In an improvement in urea synthesis, the pressure of the synthesis effluent stream is initially decreased under substantially adiabatic conditions. This results in the formation of an initial gaseous phase which consists mainly of NH_3 derived from the excess NH_3 present in the effluent stream. The initial gaseous phase will also contain a small amount of CO_2 derived from ammonium carbamate decomposition. This initial gaseous phase is separated from the residual liquid phase, which is then heated to generate an off-gas of relatively low NH_3 content, derived mainly from ammonium carbamate decomposition. This off-gas is then separated from the residual liquid phase and is utilized as the reactant gas stream which is contacted with an aqueous absorbent in a heat recovery sequence. The method conserves heat energy.

(*ibid*)

Urea Synthesis

Nobuo Zen, et al (to Sumitomo Chemical Co.Ltd.).

U.S., 3,531,521, Sept. 29, 1970, Appl. Japan, Feb. 15, 1966; 6 pp.

A method is described for recovering heat energy and recycling unconverted starting materials in the synthesis of urea from NH_3 and CO_2. The product of the synthesis reactor is decreased in pressure by an ejector. The unconverted gaseous materials are then separated from the reaction product by multistage decomposition steps. The gas separated from the second stage decomposition is recycled to ejector, together with the gas separated in the first stage. The gas mixture is then absorbed in a liquid at a higher temperature and pressure. The heat generated by the absorption is utilized to decompose the ammonium carbamate. The amount of unconverted gaseous raw materials to be separated and absorbed at a low pressure stage is decreased by the recycling of the separated gas from the second stage decomposer to the ejector.

(*ibid*)

Urea Synthesis

Guido Giommi

U.S., 3,530,180, Sept. 22, 1970, Appl. Italy Sept. 15, 1966; 5 pp. .

In the method for synthesis of urea from NH_3 and CO_2 at high temperatures and pressures wherein the portion of ammonium carbamiate which is not converted into urea is split into its components by distillation, an improvement consists of condensing the split products from the distillation step to form liquid carbamiate. The liquid carbamiate is separated from the excess NH_3 and recycled to the urea synthesis converter. The NH_3 is recycled to the distillation zone and at least a part of the CO_2 charged into the synthesis to the gases withdrawn from the distillation zone before their condensation. This modification conserves raw materials, requires less power, and gives higher yields compared with usual methods.

(*ibid*)

Production of Polyphosphoric Acid

Klaus Beltz, et al (to Knapsack-Griesheim A. G.).

U.S., 3,526,482, Sept. 1,1970, Ger. Appl. Aug. 5, 1961; 5pp. Division of U.S., 3,387,929.

Apparatus is described in which P is burned in air and the combustion products are passed successively through two absorption zones. In the first zone the combustion products are contacted with phosphoric acid containing 76-77.5% P_2O_5; in this zone 40-60% of the P_2O_5 in the combustion products is adsorbed. The gas leaving the first zone is fed to a second absorption zone where it is contacted with phosphoric acid containing 77.5% P_2O_5 to absorb the remaining P_2O_5. The acid produced in the second zone contains 84% P_2O_5. The acid concentrations in both zones are regulated by adding water or dilute phosphoric acid. The apparatus consists of two cone-shaped concentric vessels lined with graphite.

(*ibid*, 4)

Production of Superphosphoric Acid

Marco Olper (to SINCAT, Societa Industriale Catanese S.p.A.).

U.S.A., 3,527,562, Sept. 8, 1970, Appl. Italy June 18, 1965; 7 pp.

Aqueous H_3PO_4 containing 30-50% P_2O_5 is sprayed into an ascending stream of hot (250-1100°) air at the bottom of a vertical conduit with flaring sides. Flow rates and temperatures are adjusted so droplets of the acid are carried upwardly by the stream of hot air while being dehydrated. In an upper part of the conduit a fluidized bed of droplets is formed owing to the decrease in the air velocity. In the fluidized bed, dehydration of the droplets continues until they are converted to superphosphoric acid. The droplets of superphosphoric acid are swept out of the top of the vessel by the air stream and are separated in a cyclone. Compared with submerged combustion, no fog of P_2O_5 is formed, and the use of relatively low temperatures and short time of heating avoids formation of insoluble polyphosphates. Corrosion is less in the present method.

(*ibid*)

Preparation of Orthophosphorous Acid

D. D. Whyte and P. F. Pflaumer (to Procter and Gamble Co.).

U.S., 3,528,772, Sept. 15, 1970, Appl. Oct. 26, 1967; 7 pp.

Phosphoric acid is prepared by dispersing P in an anhydrous organic medium such as sulfones $(C_3H_9)_2SO_2$ or ether $(C_4H_9)_2O$ containing an aliphatic carboxylic acid such as formic or acetic acid having up to six C atoms, introducing an oxidizing gas such as air or O_2 at 50-90°, and hydrolyzing the phosphite intermediate reaction product by adding at least six mols H_2O/mol P. The hydrolysis must begin before the occurrence of any rearrangement of the intermediate product to a product containing C-P bonds. When the oxidation step is complete, the temperature drops sharply. A waiting period which elapses between the time of completion of oxidation to the start of hydrolysis can equal but must not exceed a time in min calculated by the equation: Time = 380—[mols p/mols aliphatic carboxylic acid × (3,770+20.6 T)] where T is a temperature in the range 20-100° at which the reaction mixture is maintained during the waiting period.

(*ibid*)

Purification of Phosphoric Acid

G. B. Shearon, G. J. Rubin, and R. E. Bird (to International Minerals & Chemical Corp.).

U.S., 3,528,771, Sept. 15, 1970, Appl. Oct. 10, 1967; 5 pp.

Crude wet-process H_3PO_4 solution from the gypsum filter, containing 25-35% P_2O_5, is collected in a storage tank. About 75% of the crude acid is sent to a first stage evaporator where the P_2O_5 concentration is increased to 37-40% which is high enough to precipitate $CaSO_4$ and other non-phosphatic impurities but not high enough to precipitate Fe-or Al-phosphates. The concentrated acid and the portion of the crude acid in the storage tank are mixed together in a settling tank. The mixture is held in the settling tank for about eight hr. and the clear acid is decanted from the sludge. The sludge is centrifuged and the liquid from the centrifuge is recycled to the crude acid storage tank. The clear acid decanted from the settling tank is sent to second and third stage evaporators where the P_2O_5 concentration is increased to 54%. The suspended solids in the product acid are about 3.83%. When the product from the first stage evaporator is transferred directly to the second stage evaporator, the product acid contains 7.82% suspended solids. Thus, the method patented decreases the solid impurities in the product acid by about 51% without significant loss of P_2O_5.

(*ibid*)

Solvent Extraction Process for the Production of Ammonium Nitrate Fertilizer Product and Phosphoric Acid Mixed with Nitric Acid

Samuel Strelzoff, et al (to Chemical Construction Corp.).

U.S., 3,518,073, June 30, 1970, Appl. Jan. 23, 1967; 6 pp.

A double-solvent technique is used to separate Ca nitrate from the H_3PO_4 in a solution made by extracting phosphate rock with HNO_3. Alcohols (isoamyl, amyl, or isobutyl) are used to extract nitrate and H_3PO_4 countercurrently; residual alcohols are extracted from the aqueous solution with water-immiscible solvents such as benzene or petroleum ether.

(*ibid*, 5)

Continuous and Rapid Production of Phosphates

J. P. Spring.

U.S., 3,510,264, May 5, 1970, Appl. Jan. 21, 1963-Oct. 12, 1967; 8 pp.

Phosphoric acid (73-85%), $CaCO_3$, and a base, such as CaO, are simultaneously and continuously introduced into a drum mixer, rotating at 10 rpm, and mixed to assure a rapid reaction between the acid, carbonate, and base. The wet slurry is then poured quickly and continuously through an opening in the drum mixer and onto a slowly moving reactor belt. As the slurry moves along the belt, it forms a reacting layer through which CO_2 is allowed to form voids in the phosphate. The speed of the reactor belt is adjusted so that when each segment of the layer reaches the end of the reactor belt it is in the form of a porous, slightly moist mass (7-8% moisture by wt). Each portion of the layer remains of the belt for 30-45 min, after which it drops into a collecting bin, breaking up into chunks as it falls. The chunks are fed into an agitating type dryer, granulated into hard, solid balls, and screened.

(*ibid*, 6)

Nitrogen-Phosphorus Compounds

H. T. Lewis (to Tennessee Valley Authority).

U.S., 3,539,328, Nov. 10, 1970, Appl. Sept. 17, 1968; 8 pp.

New high-analysis NP compositions suitable for fertilizer use are prepared by vapor phase reaction of NH_3,O_2 and elemental P in a two-stage reactor. The temperature in the first stage is 950-1066°F. and that in the second stage is 1200-1600°F. In the first stage, vapors of NH_3,O_2 (as dry air). and P are introduced at rates to provide a 120-300% excess of O_2 over that required to give an O_2:P_4 mole ratio of 5:1. The NH_3 is introduced at a rate to provide 60-280% of that required to give an N:P atomic ratio of 2:1. The residence time in the first reactor is 1-7 seconds. The reaction gases from the first reactor are fed to the second stage where the residence time is 0.5-4 seconds. The product from the second stage is cooled, and collected in the form of an amorphous, white, particulate solid which is substantially nonhygroscopic. The degree of water-solubility can be regulated between 20 and 95%. The N content is 12-20% and the P content is 34-41%.

(*ibid*)

Nitrophosphate and Ammonium Nitrate-Calcium Carbonate Fertilizers

J. F. Villiers-Fisher and A. J. Andreatch (to Chemical Construction Corp.).

U.S., 3,518,071, June 30, 1970, Appl. Jan. 23, 1967; 6 pp.

A product-recycle technique is combined with solvent extraction in separating Ca nitrate from the H_3PO_4 in a solution made by extracting phosphate rock with HNO_3. The process consists of the steps: (1) countercurrently extracting the nitric phosphate extract with an alcohol such as isoamyl, amyl, or isobutyl, (2) countercurrently extracting the organic solvent phase from step 1 with a solution of NH_4NO_3 and ammonium phosphate recycled from step 7, (3) recycling the solvent fraction from step 2 to step 1, (4) reacting the aqueous fraction from step 2 with NH_3 to form the nitrate and phosphate, (5) evaporating the solution from step 4 to crystallize out part of the ammonium phosphate, (6) separating the crystals from step 5 to give ammonium phosphate, (6) separating the crystals from step 5 to give ammonium phosphate as product, and (7) recycling part of the solution from step 6 to step 2. The Ca nitrate in the aqueous fraction from step 1 can be converted to NH_4NO_3, if desired, by reacting with NH_3 and CO_2.

(*ibid*, 8)

Stabilizing Liquid Fertilizers

E. L. Stauter.

U.S., 3,527,591, Sept. 8, 1970, Appl. Feb. 14, 1968; 2 pp.

Kelp meal is a suspending agent and crystallization inhibitor for liquid fertilizers. For example, 42.9 parts of a mixture of solid $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ (having a P_2O_5: N wt ratio of 3:1), 34.8 parts of solid urea, and 38.4 parts KCl were added to 79.9 parts of water at 200°F. The batch was stirred until the solids were dissolved. While still hot, and before any crystallization had occurred, 1.9 parts of kelp meal, finely divided (10-200 mesh), was well-mixed with the hot liquid. After cooling to room temperature (68°F.) and storing for extended periods, there was no significant crystallization, compared with significant crystallization in control samples prepared without kelp. The nominal grade of the liquid was 12-12-12.

(*ibid*, 10)

Technical Urea Uses

Urea's major uses are as nitrogenous fertilizers. It is also being used as animal feed supplement. In addition to these urea has important technical applications in the production of thermosetting resins both directly and indirectly via the formation of melamine. Direct combination of urea with formaldehyde gives a series of urea-formaldehyde resins, but indirectly urea is converted into melamine which is then formed with formaldehyde into another series of resins. Urea-formaldehyde resins

are prepared by reacting urea and formaldehyde in a two stage process in the presence of pyridine, ammonia or certain alcohols. Both the heat and pH are controlled carefully to form intermediates that are then mixed with fillers to produce moulding powders. These are converted to the thermosetting resins by further controlled heating and pressure in the presence of catalysts. Urea-formaldehyde resins are strong and rigid, free of odour and taste and have excellent light diffusion characteristics. Uses of these resins include textile finishes mouldings such as tableware, light reflectors and baking enamels.

Production of melamine from urea is much cheaper and less complicated. Melamine is one of the raw materials required to make a series of melamine-formaldehyde resins which have valuable physical properties. The resins are very widely used as moulding compounds with alpha-cellulose or mineral powders as fillers and also incorporating a colouring agent, other uses include laminating, boil proof adhesive, textile treatment to adhesive crease and wrinkle resistance, and for the treatment of paper to increase its wet strength. Urea hydrogen peroxide in aqueous solution breaks down to give urea and hydrogen peroxide and can be used for any of the applications in which the use of hydrogen peroxide is traditional. It is particularly suitable for use in the pharmaceutical and cosmetic industries as a general antiseptic and deodorant, as a bleaching agent for hair dyes. It is also used as a laundry bleach and in the plastics industry to assist condensation in urea-formaldehyde resins.

Dimethyloethylene urea is manufactured by a two stage process: the first one consists of condensing excess ethylene diamine with urea to form ethylene urea with the evolution of by-product ammonia which is absorbed in a tower. The reaction mixture is heated to about 250°C during which time excess ethylene diamine distils off and is recycled to the process. Ethylene urea is formed in high yield and the molten product goes on to the second stage of the process. In this stage ethylene urea is condensed with formaldehyde at 60°C to give a 50% aqueous solution of DMEU which is treated with charcoal in a recycle process until a water-white solution is obtained. DMEU is used to impart a crease-resistant finish to textiles.

Urea is used as a de-icing, agent. In the airport run-way de-icer urea has the advantage of being non-toxic, non-corrosive and will not affect rubber, hydraulic equipment, metals, cement or any other materials connected with aircraft or airport facilities. Urea becomes effective almost immediately upon application and is good for three or four days, afterwards reacting with any new snow or stopping recurrent freezing. Application of the compound can be made from a low-flying light aircraft which is able to work under adverse conditions.

Extractive crystallization with urea: n-paraffins containing more than five carbon atoms are occluded in the channels of urea crystals to give a solid adduct, but crystalline adducts are not formed with most branched chains or ring type hydrocarbons. Use is made of urea when separating specifically n-paraffins from hydrocarbon fractions. The nature of urea n-paraffin complex is such that the crystals are stable and easy to handle and many can be decomposed readily for recovery of the extraction fraction and urea which can be recycled in the process.

In hospitals, urea is used to remove excess body fluids, and it has an amazing ability to shrink the brain, relieving pressure before brain surgery. Its most important medical application, however, is for external treatment of certain types of wounds. Urea dissolves dead tissue in which bacteria thrive and the wound is more easily healed.

Recent studies carried out at Chicago University show that urea is a very promising rain inducer. When dropped on heavy layers of stratus clouds 3,000-6,000 ft. high, it effectively triggered the release of snow. Research scientists predict that urea would be just as effective on summer clouds to produce rain.

(Nitrogen No. 67 Sep/Oct. 1970, 33)

News in Brief

Development in Food Technology

Mysore's Central Food Technological Research Institute (CSIR) has won the coveted industrial achievement award of the Institute of Food Technologists of USA for 1971 in recognition of the significant advance made in the application of food technology to industrial production which can help solve the food problem. This is the first time that an award has been made to an institution outside USA.

Milktone, the subject of the award, is a protein drink, prepared from groundnut and hydrolysed starch, which saved on imported milk powder. This new drink is being produced and marketed in Bangalore with the cooperation of the Government-owned dairy. UNICEF and several state governments have shown interest in setting up commercial plants for its manufacture. It has more proteins and vitamins than milk. It is a good substitute for skim milk powder used by dairies in the production of toned milk.

[*CSIR News*, **21** (12) (1971), 92]

Integrated Water Management

A 2-day seminar on Soil and Water Management held at Ranchi in early May 1971 recommended that integrated water management should be planned and executed in the command in a compact manner involving land sharing and grading construction of lined field channels and underground pipe for water conveyance and land drainage. The technical deliberations of the various groups and their recommendations included the following: (i) drainage be made an integral part of the project reports of the river valley projects in future, (ii) emphasis on soil and water resources as national assets for careful protection and economic use, (iii) close coordination between the various departments of Soil Conservation and Minor Irrigation Revenue for selection on priority to sub-catchments and intergrated planning.

The most significant recommendation was that since the core of the dry farming programme was the soil and water conservation, the programme should be implemented by the soil conservation organization in Bihar as in other states.

Outlays on Research

The Ministry of Industrial Development, Govt. of India, is of the view that companies importing foreign technology should necessarily prescribe minimum resources outlays on research and development, at least as much as the cost of imported know-how during the period of collaboration.

In view of individually large companies having investments over Rs. 5 crores, the investment on research and development (R & D) could perhaps be linked to the overall profits in a year. The Ministry has commended these views to the members of the standing committee of the Central Advisory Committee on Industries. Restricting import of technology is not favoured by the Ministry as no country can today afford to isolate itself from technological development in the rest of the world. At the same time, a positive approach for ensuring greater indigenous R and D is extremely necessary, for propagating of which or in ensuring commercial utilization of research results management and industry support is an essential precondition.

Tata Fertilizer Project

The Rs. 55 crores project at Mithapur (Gujarat) for the production of 900,000 te/yr of high analysis basic fertilizer materials, containing 406,000 te of balanced plant nutrients, is understood to have been cleared by the Union Government. Of the capital cost, Rs. 25 crores will be in foreign exchange. The Government had issued the letter of intent on July 25, 1970 subject to two conditions, viz. (i) that the company would obtain clearance under the Monopolies and Restricted Trade Practices Act which came into force on June 1, 1970 and (ii) import of phosphoric acid for 5 years would be permitted subject to the condition that it was proved to the satisfaction of the Government that the import of phosphoric acid involved lower foreign exchange than that would be needed for the import of raw materials required for its manufacture in the country.

The sponsors were told that the likely availability of rock phosphate from the indigenous sources should be kept in mind. Further, if the import of phosphoric acid was allowed, its price and terms of contract would be subject to the approval of the Government. Also the factory should establish facilities in India for the production of phosphoric acid at the end of 5 years if so required by the Government in advance.

[*FAI Inf. Serv.*, **12** (10) (1971), 7]

Rock Phosphate in Rajasthan

The Chief Minister of Rajasthan, Sri Sukhadia, said at Udaipur recently that the World Bank was inclined to give all possible help in the development of rock phosphate mines in Rajasthan. The development of the mines to extract more rock phosphate daily would go a long way in saving foreign exchange. The Jhamar Kotra reserves had the finest quality, whereas 'D block' had rock phosphate with 32 per cent P_2O_5. The daily production from Jhamar Kotra would rise from the present 1000 tonnes to 10,000 te by 1975; the country's requirements of rock phosphate would then be roughly 3 crore tonnes. The transportation arrangement in that area has to be improved.

[*ibid*, 8]

Methane from Coal

The world's first plant designed to convert coal to a clean-burning synthesis gas, cosponsored by the Office of Coal Research

and the American Gas Association, will use the HYGAS process developed by the Institute of Gas Technology. The pilot plant is designed to consume 75 tons of coal/day and produce 1.5 MMCf of gas. The commercial plant, which will go into operation by 1977, would produce about 250 MMCf of gas.

Coal is crushed into particles of table salt size and moisture is removed. Next, air heated to about 800°F is blown through the particles which are then combined with right oil to produce a mud-like mixture. Coal in this form is injected into the top of the hydrogasification reactor under a pressure of 1000-1500 psi. As it falls methane is formed which rises. Upon reaching the top of the reactor the gas temperature is about 600°F. It is then cooled and passed through a purification solution. At this stage about two-thirds of the gas has been converted to methane; the remaining conversion is accomplished by passing the purified gas mixture through a methanation stage.

(Source: Hydrocarbon Processing, Nov. 1970)
[*Oil Commentary*, **8** (6) (1971), 10]

Corrosion Map of India

The Corrosion Advisory Bureau of the CSIR Metals Research Committee has brought out a publication wherein the rates of corrosion of mild steel and zinc determined at 26 places in the country over a period of 5 years (1963-68) have been mapped. Six maps included in the book show areas found by the same range of corrosion rates and relate to: (i) maximum and minimum monthly corrosion rates, (ii) yearly corrosion rate and (iii) monthly corrosion rates Nov. to February, March to June and July to October. A complete record of rate of corrosion under different climatic and pollutional conditions is also given.

The rate of corrosion was found to vary from region to region and the intensity of attach was more in the industrial areas and along the sea coast. The data indicate an interplay of pollution, meteorological conditions and other factors on the rate of corrosion. At Digha (W. Bengal sea coast) the corrosion rate was maximum before the onset of rains; with the commencement of rains the extent of corrosion decreases appreciably along with the pollution level in the atmosphere. Various regions have been grouped into 5 categories, viz. very high (> 0.25 mm/yr); high (0.13-25 mm); moderate (0.05-0.13 mm); low (0.025-0.05 mm) and very low (< 0.025 mm.). Broad guidelines in regard to protective measures to be used for combating corrosion in the regions categorized are also provided in the form of a chart which would be of considerable use in the selection of suitable coatings.

[*CSIR News*, **21** (9) (1971), 1]

Foodgrains Loss in Storage

An expert committee has estimated that loss to foodgrains in storage in India may come upto 6 per cent taking into account all the stocks held by farmers, traders and other stockists, according to Sri A.P. Shinde, Minister of State for Agriculture. In respect of stocks handled by the food Corporation of India and the Central Warehousing Corporation the losses are within 1 per cent of the quantity stored.

[25.6.71]

Fertilizer Intake below Target

According to Sri A. P. Shinde, Minister of State for Agriculture, Government of India, there was a shortfall of 18 per cent in the consumption target for fertilizer during 1970-71. The shortfall in the previous two years was 37 and 23 per cent respectively. The main reasons for the low level of consumption in comparison to targets were natural causes like cyclones and floods in some States, constraints in the availability of credit for fertilizer distribution and use, inadequacies in the fertilizer distribution arrangement, gaps in extension and promotional efforts and unfavourable price ratio between inputs and the produce.

The Government had recently set up a credit guarantee corporation to encourage banks to provide greater credit facilities to farmers and dealers of fertilizers. It was also considering the setting up of a fertilizer promotion council as a joint venture among the Central and State Governments, agricultural unversities and fertilizers manufactures to supplement the promotional measures undertaken by the State governments and manufacturers.

[*FAI Inf. Serv.*, **12** (12) (1971), 5]

Konkan Fertilizer Plant

The decision of the Government of India to give clearance to the Rs. 35 crores fertilizer project will go a long way to give fillip to the Maharashtra Government's new Bombay scheme envisaging the setting up of a twin city across the harbour. The plant is proposed to be set up at Nhava Sheva, (Colaba district), which is proposed to be developed by the State Government as new Bombay's premier port.

The promoters foresee an output of 250,000 tonnes of fertilizers within the first year of setting up of the plant. It will produce half a million tonne after 4 years and will help save foreign exchange to the tune of Rs. 25 crores. When complete, it will have a daily capacity of producing 2000 tonnes of sulphuric acid, 750 te of phosphoric acid and 1500 te of diammonium phosphate as well as NPK fertilizers. The Government of India is reported to have made it known that it might review the question of importing ammonia after 7 years.

[*ibid*, 7]

Pressure Gasification of Indian Coals

With a view to preparing town gas and synthesis gas and their possible integration with fertilizer and synthetic oil industries and low temperature carbonization plus pig iron manufacture, Central Fuel Research Institute has studied some of the typical non-coking coals of Talcher (Orissa), Raniganj (W. Bengal), Singareni (AP) and Sohagpur (M.P.) in its fixed-bed pressure gasification pilot plant using steam and oxygen as the gasifying media. These tests established the amenability of Indian coals to pressure gasification. In spite of the low initial deformation temperature of the ash of coals tested, no operational difficulty was encountered. From a broad spectrum of the gasification characteristics of the different non-coking coals, correlations have been established between plant pressure and gasifier performance as judged from the values of gas yields and quality, percentage of carbon gasified and percentage thermal efficiency for the coals tested. It would now be possible to predict with a fair degree of accuracy the expected performance figures of even untried fuels under a set of known operating conditions.

The tar obtained during gasification can either be processed to valuable end-products or sold out at a reasonable rate. But in the event it is desired to increase the synthesis gas yield in lieu of tar, this can be achieved by recycling back the heavy tar to the gasifier and reforming the light tar with crude gas in a reformer.

The pilot plant studies have porvided valuable information and pertinent process data for the preparation of project reports for the establishment of commercial pressure gasification plants in the country.

[*Ind. J. Technol.*, 9 (1971), 63]

Technical Manpower

The Colombo Plan Bureau organized a colloquium on Intra-Regional Technician Training and Migration of Scientific and Technical Personnel at Manila during March 2-6, 1971 under the chairmanship of Brig. General A. B. Connelly, Director of the Bureau. The colloquium was inaugurated by O. D. Corpuz, Secretary of Education, Government of the Philippines, and the discussions centred around the following papers: (1) Some Aspects of Intra-Regional Technician Training by Irshad H. Khan (2) Technical Education and Training in a National Plan for Technical Education and Training by T. O. P. Fernando, Ceylon (3) Administration of Technician Training Programmes at the National, Provincial and Institutional Levels by W. M. Robertson, Australia (4) Administration of Technician Training Programmes at the National, Provincial and Institutional Levels by H. F. Belen, Philippines (5) The Importance of Technician Teachers, Physical Facilities, Administrators and Ancillary Staff for Developing Technician Education and Training by J. W. Gailer, U.K. (6) The social and Language Barriers to an Expansion in Technician Education and Training in the Region by Barnard, (7) Impact of the Migration of Scientists, Engineers, Technicians and Technical Teachers on Development Programmes of a Developing Country by Kamalesh Ray, CSIR, New Delhi. A day was devoted to discussions in depth of the important questions arising from the papers presented by consultants.

It was felt that there was generally want of adequate data on migration of scientists, engineers, doctors, etc. from developing countries. The figures of Indian scientific and technical personnel abroad and and assessment of the Brain Drain from India were highly appreciated. The most acceptable way of minimizing the Brain Drain, the colloquium observed, would be the socio-economic development of the countries of the Region so that they could profitably absorb all the skilled manpower produced.

The technicians seek employment in the other types of jobs or try to acquire higher education to become technologists and engineers. So sufficient social recognition and economic incentives be provided so that the technicians can go up the service later to a reasonable height. Similarly, teachers in the training centres should also get adequate recognition and service conditions in the salary structure of the country.

[*Tech. Manpower* (*CSIR*), **13** (4) (1971), 1]

Indian Standards

Indian Standards Institution has prepared the following draft specifications for: (1) urea (technical) Doc: CDC 24 (3952) and (2) sodium pentachlorophenate, technical DOC CDC4 (5457). In the specification (1) the biuret content has geen substantially reduced to meet the needs of the consumers and additional requirements have been included for controlling the quality of the product. The specification caters to the needs of the plastics and the adhesives industries which are at present the major consumers of technical grade urea.

The specification (2) prescribes the requirements and methods of sampling and test for chlorophenates, moisture, free alkalinity and colour of the acqueous solution. The material is used as a weedicide, fungicide, preservative, white antrepellent and as a fermentation disinfectant.

[*J. Mines, Metals & Fuels*, **19** (4) (1971), 116]

Nitrogen Bibliography

The European Nitrogen Service Programme, a non-commercial, non-profit fertilizer service organisation has undertaken a project to compile all the literature published on research pertaining to nitrogen in Indian agriculture from 1960 onwards.

The project is intended to cover nitrogen research in its broadest sense including crop science, soil science, agricultural economics, microbiology, biochemistry, physiology, fertilizer handling and marketing and fertilization of all crops.

The organization requests all the scientists to send their own published work and any reprints, reports, thesis titles and bibliographies for inclusion in the bibliography.

FCI's Agreements/Contracts with Foreign Firms

(1) Fertilizer Corporation of India signed an agreement with M/s Fredrich Uhde GmbH of Dortmund (W. Germany) for carrying out the highly specialized job of unloading ammonia directly from a ship berthed at Bombay. Using imported ammonia as feedstock for expansion, Trombay unit will acquire additional production capacity of one million tonnes of fertilizers at a cost of Rs. 44 Crores. Ammonia is to be kept at a constant temperature of −33°C while handling it from the ship to the storage tank and taking it from the tank to the plant. The 15,000 tonnes capacity storage tank, which will keep ammonia under proper refrigerated conditions, will be the largest so far set up in India.

Ammonia will be taken from the tank to the plant through a 5-km pipeline. Ammonia will be imported from Iran and Kuwait. (2) Arrangements have been made for import of special raw material required for fabrication of structures at FCI's Ramagundam project. Contracts have been signed with suppliers of machinery and equipment in Italy, Germany and Czechoslovakia. By the end of 1972 the machinery worth Rs. 23 crores is expected to arrive in India. For supplier's credit, contract with Montedison (Italy) and Czechs have been concluded, whereas a Letter of intent has been issued to Koppers (W. Germany). The licence and know-how agreements have also been entered into.

[*Fertil. Digest*, 9 (4) (1971), 19]

Modernization of Sindri Fertilizer Works

The 20-year old fertilizer factory at Sindri will be modernized at a cost of Rs. 95 crores, of which over Rs. 25 crores will form the foreign component. After its completion, the project will yield additional 1,70,000 tonnes of nitrogen, which will be in the form of 40,000 tonnes of additional ammonium sulphate and 3,79,000 tonnes of additional urea.

The proposed project, now being finalized, will be based on the partial oxidation of petroleum feedstock, like LSHS/HSHS, which will be obtained from the proposed Bongaigaon refinery at Assam. The new plants when completed will have the capacity of producing 900 tonnes of ammonia and 1200 tonnes of urea per day. The fertilizers will yield an additional yearly sale of over Rs. 25 crores. The annual saving in foreign exchange will amount to Rs. 19 crores and the percentage of return on the total capital invested would be 7.60.

With the possibilities of obtaining LSHS

from Bongaigaon or in the event of its diversion to Barauni, HSHS from Barauni has been considered as feedstock to replace the use of coal. When this proposal is approved, the coke oven and semi-water gas generation will be discontinued.

[*Fertil. Digest*, 9 (4) (1971), 9]

Indian Know-how for Brazil

The Fertilizers and Chemicals (Travancore) Ltd. (FACT), a public sector undertaking, has provided the technical know-how, basic design and engineering assistance to set up a 10 tons/day ammonium chloride plant for Engechlor Industries Quimica, Rio de Janeiro. This plant has started production and chemically pure ammonium chloride was produced for the first time in Brazil in March 1971, the capacity being 3000 tonnes/yr.

[*Fertil. Digest*, 9 (4) (1971), 17]

Rationalization Projects at Sindri

Recently Government of India has given green signal to the Rationalization Project for the Sindri Unit of FCI Ltd., under which a triple superphosphate plant, designed by the Planning and Development Division FCI, will be erected at an estimated cost of Rs. 35 crores using rock phosphate—either imported or available indigenously—and sulphuric acid. While the by-product gypsum will be sent to the existing sulphate plant for production of ammonium sulphate, phosphoric acid will be further treated with rock phosphate to produce triple superphosphate with P_2O_5 content 46-48 per cent.

The sulphuric acid will be produced from indigenous pyrites (Fe_2S 33 per cent), thereby making the project independent of imported sulphur. There will be two plants —a 400 te/day plant put up by Simon Carves, the other 800 te/day to be set up by Techno-Export, Bulgaria—both using fluidized-bed technology.

The phosphoric acid plant in being put up in collaboration with FEDO—the design unit of FACT—using Prayon process. On completion of the project, 346000 te of triple superphosphate will be produced every year.

The production pattern at Sindri after completion of the rationalization scheme is as follows:

Product	Capacity, te/yr.
Ammonium Sulphate	3,10,000
Urea	21,000
Double Salt/NPK Granulation Scheme	72000/60000
TSP	3,46,000

[*Fertilizer Digest*, 9 (4) (1971), 6]

Ammonium Nitrate Plant at Sindri

The construction work of a 30 te/day ammonium nitrate plant has been inaugurated. Expected to be commissioned by September 1971, this plant will be the first of its kind in India to produce 9,000 te/year of prilled ammonium nitrate for use in various types of explosives required in mining and other industries. Estimated to cost Rs. 43 lakhs, the plant has been designed by the engineers and technicians of FCI based on their own know-how.

[*Fertilizer Digest*, 9 (4) (1971), 24]

STATISTICS

TABLE 1—CURRENT PRICES OF FERTILIZERS**, RS./METRIC TON

Fertilizers	Pool Price For			Distribution Margin For			Maximum Retail Price
	States	Plantation	F.C.I.	States	Plantation	F.C.I.	
Imported and Indigenous Statutorily Controlled							
1. Ammonium sulphate							
— White	474	499	474.00	55	30	55	529+
— Coloured	374	399	374.00	55	30	55	429+
2. Ammonium sulphate nitrate	564	1593	570.20	62	33	55.80	626+
3. Urea-46% N grade	843*	883*	851.00*	80	40	72	923‡+
4. Calcium ammonium nitrate							
— 20.5% N grade	421	442	—	52	31	—	473+
— 25% N grade	490	514	—	55	31	—	545+
Imported—Pool							
5. Ammonium chloride	484	—	489.50	55	—	49.50	539
6. Calcium ammonium nitrate — 23% N	430	—	—	55	—	—	485
— 26% N	515	544	521.00	60	31	54	575
7. Ammonium phosphate (20-20-0)	814	—	822.00	80	—	72	894
8. Ammonium nitrophosphate (20-20-0)	800	—	808.00	80	—	72	880
9. Diamonium phosphate (18-46-0)	1,122	1,172	1,131.50	95	45	85.50	1,217
10. N. P. K. Mixtures							
— (13-13-13)	710	—	717.00	72	—	65.00	782
— (14-14-14)	755	—	762.50	75	—	67.50	830
— (12-24-12)	830	—	838.50	85	—	76.50	915
— (15-15-15)	832	—	840.00	80	—	72.00	912
— (14-28-14)	1,047	—	1,056.00	90	—	81.00	1,137
— (10-26-26)	1,025	—	—	—	—	—	—
— (12-32-12)	1,045	—	—	—	—	—	—
— (14-36-12)	1,135	—	—	—	—	—	—
11. Dicalcium phosphate—28% P_2O_5	455	—	—	55	—	—	510
12. Muriate of Potash (61% K_2O)	483	—	487.00	40	—	36.00	523
Imported—IPSA							
13. Muriate of Potash—(60% K_2O)	483.00 f.o.r. dispatching station freight						
—(50% K_2O)	403.00 prepaid to destination station.						

*With effect from 4th March 1971

‡With effect from 9th March 1971

**Includes excise duty (10%) on fertilizers with effect from 1st March 1969

+Retail prices are statutorily controlled.

Note: F.C.I. = Food Corporation of India Limited.

(*FAI Inf. Serv.*, **12** (7) (19171), 9)

TABLE 2—WORLD CAPITAL AND EXPLORATION EXPENDITURE IN PETROLEUM INDUSTRY* (1969)

(In million dollars)

Region/country	Production	Transportation		Processing		Marketing	Others	Total Capital Expenditures	Exploration	Grand Total
		Pipelines	Marine	Refineries	Chemical plants					
U.S.A.	4,750	300	100	950	575	1,250	250	8,175	725	8,900
Canada	750	50	10	150	50	150	15	1,175	175	1,350
Venezuela	225	15	—	95	—	5	—	340	20	360
Other Western Hemisphere	335	25	10	400	175	100	55	1,200	75	1,275
Western Europe	275	75	10	850	350	825	95	2,480	125	2,605
Africa	575	100	—	90	—	50	—	825	85	910
Middle East	330	210	5	100	10	25	50	730	50	780
Far East	300	25	5	575	150	400	45	1,500	125	1,625
Unallocated	—	—	1,950	—	—	—	—	1,950	—	1,950
World Total	7,540	910	2,090	3,210	1,310	2,805	510	18,375	1,380	19,755

*Excluding Soviet Bloc.

Source: The Chase Manhattan Bank.

(*Oil Statistics*, **8** (4) (1970), 7)

TABLE 3—MANPOWER EMPLOYED IN THE PETROLEUM INDUSTRY IN INDIA
(As on 1st April of each year)

(Numbers)

Category	1965	1966	1967	1968	1969	1970
Exploration & Production	19,399	21,559	22,248	23,876	25,369	26,465
Refining	9,566	9,672	9,998	10,252	10,539	10,528
Marketing	24,305	23,687	23,132	22,234	21,353	20,549
Others:						
I.O.C. (Pipelines)	345	454	400	524	484	
O.N.G.C. (Pipelines)	n.a.	n.a.	156	162	177	
O.I.L. (Pipelines)	—	—	—	438	443	1,864
I.I.P. (Research)	291	305	510	512	545	
Grand Total	53,906	55,645	56.444	57,998	58.910	59,406

Note: Total does not include staff employed on contract basis.
Included already in exploration and production staff.

(*Oil Statistics*, **8** (4) (1970), 13)

TABLE 4—CAPACITY AND PRINCIPAL SALEABLE PRODUCTS OF INDIA REFINERIES UNDER OPERATION

	Private Sector				Public Sector				
Name of Refinery	AOC	Burmah-Shell	ESSO	Caltex	Gauhati	Barauni	Koyali	Cochin	Madras
Installed Capacity, million tonnes	0.5	3.75	2.75	1.25	0.80	3.00	3.4	2.5	2.5
	Mogas	Mogas	Mogas	Mogas	Mogas	Mogas	Mogas	Mogas	Fuel gas
	Kerosene	Kerosene	Kerosene	Kerosene	Kerosene	Kerosene	Kerosene	Kerosene	L.P.G.
	Diesels	Diesels	Diesels	Diesels	Diesels	Diesels	Diesels	Diesels	Naphtha
	Furnace oil	Furnace oil	Furnace oil	Furnace oil	Furnace oil	Furnace oil	Furnace oil	Furnace oil	Gasolene
	Bitumen	J.B.O.	J.B.O.	Bitumen coke	Petroleum	Bitumen	L.P.G.	Bitumen	Kerosene
	Lubricating oil	Bitumen	Bitumen	L.P.G.	Iomex	L.P.G. naphtha	Naphtha	Naphtha	Diesels Gas oil
	Petroleum coke	L.P.G.	L.P.G.	Naphtha	A.T.F.	Petroleum coke	A.T.F.		Tar
	Aromex	Naphtha	Naphtha	Mineral turpentine		Mineral turpentine			Lube stock
	Vapourising oil	Hexane	Hexane	A.T.F.		J.P.A.			Wax
	Paraffin wax	S.B.P. spirit	S.B.P. spirit			A.V. gas components			
	Malariol	Mineral turpentine	Mineral turpentine			Lubricating oil			
	Solar oil	Carbon black	Carbon black						
	Mineral Jelly	A.T.F.	A.T.F.						
	Earth oil	Feedstock	Feedstock						
	Special heavy kerosene oil	A.V. gas components							
		Motor gasolene components							

(Source: Report, 1969-70, Deptt. of Petroleum and Chemicals, Government of India).

(*Mines and Minerals*, 7 (1970), 103)

TABLE 5—PHOSPHATE RESOURCES OF SOME COUNTRIES

Country	Million long tons of P_2O_5
Franch Morocco	21,000
U. S. A.	14,500
U. S. S. R.	7,600
Tunisia	2,000
Algeria	1,000
Brazil	600
Peru	450
U. A. R.	200
Togo	120
Spanish Sahara	100
Indian and Pacific Ocean Islands	40
Senegal	40
India	76*
Other Countries	700

(+*Of rock phosphate)

(Balasundaram, M. S., *Eastern Metal Rev.* **24** (Ann. No.) (1971), 70)

TABLE 6—POTASH IMPORTS DURING 1963-64 TO 1967-68

Year	Imports in terms of K_2O 0, tonnes	Total Cost, million Rs.	Price/tonne (Approx. & average), Rs.
1963-64	64,010	30.41	475
1964-65	57,176	28.72	502
1965-66	93,641	46.35	495
1966-67	1,44,657	76.51	524
1967-68	2,60,123	170.30	655

(Balasundaram, M. S., *Eastern Metal Rev.*, **24** (Ann. No.) (1971), 77)

TABLE 7—PRODUCTION AND IMPORT OF ROCK PHOSPHATE IN INDIA
(tonnes : '000 Rupees)

Year	Andhra Pradesh Qty	Bihar Qty	Tamil Nadu Qty	Rajasthan Qty	Total Qty	Total Value	Import (natural) Qty	Import (natural) Value
1960	1,145	13,627	149	—	14,921	486	244,244	21,099
1961	642	19,498	—	—	20,140	593	233,351	21,069
1962	1,287	27,731	—	—	29,018	853	287,721	24,857
1963	1,277	11,850	—	—	13,127	406	297,687	24,168
1964	647	3,402	—	—	4,049	143	449,407	38,750
1965	972	6,104	—	—	7,076	304	494,754	48,893
1966	2,955	13,322	—	—	16,275	665	849,774	113,731
1967	6,520	5,111	—	—	11,631	631	602,930	96,511
1968	6,430	265	—	—	6,695	523	860,625	125,435
1969	7,071	2,245	—	69,175	78,491	6,772	661,747	90,359

(Balasundaram, M. S., *Eastern Metal Rev.*, **24** (Ann. No.) (1971), 71)

TABLE 8—CRUDE OIL PRODUCTION IN INDIA, 1960-69

Year	Quantity	Value (Rs. '000)
1960	454,000	22,700
1961	513,000	32,900
1962	1,078,000	72,200
1963	1,652,000	112,600
1964	2,212,000	149,300
1965	3,022,000	204,800
1966	4,647,000	405,200
1967	5,667,000	534,800
1968	5,853,000	551,224
1969	6,723,000	672,400

(*Source*: Mineral Statistics of India, Indian Bureau of Mines, Nagpur)

(*Mines and Minerals*, **7** (1970), 101)

TECHNOLOGY Vol. 8 (1971), No. 3, July-September

The following papers, short communications and research note have been accepted for publication in TECHNOLOGY, **8** (1971), No. 3, July-September.

Papers

EFFECT OF γ-ALUMINA IN REFORMATION CATALYST: STUDIES ON ACTIVITY AND STABILITY
by D. K. Mukherjee, J. Misra, S. P. Sen and K. R. Chakravorty

RELATIONSHIP BETWEEN SURFACE AREA AND TEMPERATURE OF SINTERING IN NiO, Al_2O_3, Fe_2O_3 AND Fe_2O_3-Cr_2O_3 SYSTEMS
by B. R. Arora, R. K. Banerjee, N. K. Mandal, N. C. Ganguli and S. P. Sen

AN APPROACH TO THE DESIGN OF SHIFT CONVERTER FROM LABORATORY DATA
by H. Mahapatra, N. Ray, Bhaskar Sen and S. P. Sen

LOW TEMPERATURE WATER GAS SHIFT REACTION: EFFECT OF PRESSURE AND PARTICLE SIZE ON THE RATE OF REACTION ON COPPER-ZINC CATALYST
by S. Ahmed, A. Sengupta, N. B. Bhattacharyya and S. P. Sen

EFFECT OF HEAT TREATMENT ON STRUCTURAL PARAMETERS AND ACTIVITY OF ZINC OXIDE
by M. S. Chhabra, V. K. Puri, P. K. Sengupta, N. B. Bhattacharyya and S. P. Sen

DETERMINATION OF SURFACE AREA OF COPPER IN A LOW TEMPERATURE SHIFT CATALYST
by G. Sengupta, H. Mahapatra, R. M. Cursetji and S. P. Sen

ROLE OF NICKEL OXIDE ON THE SINTERING BEHAVIOUR OF NiO-Al_2O_3 CATALYSTS
by D. K. Mukherjee, H. Roy, S. K. Adhya, N. Bahadur and S. P. Sen

POLAROGRAPHIC STUDY OF COPPER, IRON AND ZINC SYSTEM IN TRIETHANOLAMINE RAPID ANALYSIS OF LOW TEMPERATURE CO-CONVERSION SHIFT CATALYST
by A. Sarkar, S. R. Naidu and S. P. Sen

AMPEROMETRIC COMPLEX-FORMATION TITRATIONS OF TRACES OF SELENIUM (IV)
by S. S. Chatterjee and B. K. Banerjee

AMPEROMETRIC DETERMINATION OF TRIVALENT ARSENIC WITH PHOSPHORUS PENTASULPHIDE
by S. S. Chatterjee and B. K. Banerjee

NATIVE FIXED AMMONIUM NITROGEN IN DIFFERENT INDIAN SOILS AND THE EFFECT OF IONIZING RADIATION ON IT
by S. C. Chatterjee, Subarna R. Upadhyay and B. K. Banerjee

ELECTRONIC AND VIBRATIONAL SPECTRA OF 2.5-: 2.6- AND 3.4-DICHLOROSTYRENES
by B. J. Ansari and I. D. Singh

STUDIES ON THE RELATIVE EFFICIENCIES OF SOIL AND FOLIAR APPLICATION OF UREA ON BRINJAL (*Solanum melongena* L.)
by N. N. Bid, P. K. Das and S. P. Dhua

STUDIES ON THE INFLUENCE OF DIFFERENT DOSES OF NITROGENOUS FERTILIZERS ON THE INCIDENCE OF PESTS IN SEVERAL VARIETIES OF BRINJAL PLANT
by D. P. Chakraborty, K. P. Das Gupta, G. C. Ghosh and S. P. Dhua

EFFECT OF DEGREE OF BASE SATURATION AND PHOSPHATE ENRICHMENT ON THE UTILIZATION OF SOIL AND FERTILIZER PHOSPHORUS IN ALLUVIAL, BLACK AND RED SOILS OF INDIA
by D. L. Deb and N. P. Datta

Short Communications

EFFECT OF AMMONIUM SULPHATE CONCENTRATION ON THE THERMAL DECOMPOSITION OF AMMONIUM NITRATE
by R. C. Saxena and S. Varma

TECHNOLOGY

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Vol. 8 JULY-SEPTEMBER & OCTOBER-DECEMBER 1971 Nos. 3 & 4

CONTENTS

The results of the studies on the activity and stability of six alumina-supported nickel catalysts having different proportions of α- and γ-alumina show that activity increases with increase in γ-alumina content of the carrier upto a certain extent beyond which the trend is reverse. Carbon liberation on the catalysts varies in the same manner as in case of activity. Stability of the catalysts is found to increase progressively with increase in γ-alumina content.

Effect of *Gamma*-Alumina in Reformation Catalyst: Studies on Activity and Stability

By D. K. Mukherjee, J, Misra S. P. Sen and K. R. Chakravorty,

Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar

Introduction

The factors affecting the activity, resistance to carbon liberation and mechanical stability of catalysts, employed in the hydrocarbon steam-reforming process, have been investigated by many workers[1–7]. All the above three aspects of a reformation catalyst are important for its satisfactory performance in a commercial reformer. Achievement of the most desirable formulation is restricted by the fact that factors responsible for higher activity may have adverse effect on other two aspects of the catalyst and *vice versa.* So, a compromise between opposing factors is always aimed at to achieve the best possible formulation.

Nickel on alumina-type catalysts are mostly employed for the purpose of hydrocarbon-steam reformation. Numerous patents[8–13] are available for the reformation catalyst formulation but not many of them fulfil all the aspects desirable for smooth running of the commercial units.

Alumina in α-phase is considered to be a better carrier for reformation catalyst than the γ-alumina due to much higher structural stability and less acidic character of the former[5]. But it is reported that γ-alumina is more active[14–16] as a catalyst carrier than α-alumina, probably due to its much higher specific surface area[17–19].

To investigate the relative effect of presence of both α- and γ-alumina in the carrier of supported nickel catalyst, several catalyst samples with different proportions of these two phases in the carrier were prepared and their structural parameters studied. The results of these studies, presented elsewhere[19], show that the crushing strength, specific surface area, porosity and pore size distribution of the supported nickel catalysts change favourably with increasing proportion of γ-alumina in the carrier. The present work deals with the effect of varying proportions of α- and γ-alumina on the activity and mechanical stability of such catalysts when used in the hydrocarbon steam-reforming process.

Experimental

Preparation of Catalyst Samples: Altogether six samples of nickel on alumina-type catalysts were prepared starting from six different alumina-carriers composed of varying proportions of α- and γ-alumina. Their preparation has been described in a previous study[19]. The six samples NA_1, NA_2, NA_3, NA_4, NA_5 and NA_6 correspond to 5, 10, 20, 40, 70 and 100 per cent of alumina in the carrier obtained from its basic carbonate. All of them contain 10 per cent of nickel by weight. The percentage of alumina from its basic carbonate in the carrier has been indicated by the term 'X' in all subsequent discussions and figures.

Activity and Stability Tests: Reformation of pure heptane in presence of steam was carried out under atmospheric pressure with each catalyst sample in a testing unit (Fig. 1). Water and heptane from respective reservoirs (V_1 and V_2) under controlled nitrogen pressure (10 cm. of mercury), flow through precalibrated flowmeters (F_1 and F_2) and enter into the vaporizer (E) heated by an electric muffle furnace. The mixed vapor of water and

naphtha leaves the vaporizer at 400°C as indicated by a thermocouple (T) connected to a pyrometer and enters the reactor (R) at the top. The reactor tube is of 20 mm. inner diam. and 300 mm. length made of high heat-resistant special steel and is heated by another electric muffle furnace. The top portion of the reactor serves as a preheater. The mixed vapour of water and heptane flows down the reactor and enters the catalyst bed (K) packed at the middle of the tube and maintained at a constant temperature. Two thermocouples (T_1 and T_2) are provided one at the top and the other at the bottom of the catalyst bed—to indicate inlet and outlet temperatures of the gas mixtures. The temperatures of vaporizer and reactor are controlled by energy-input regulators.

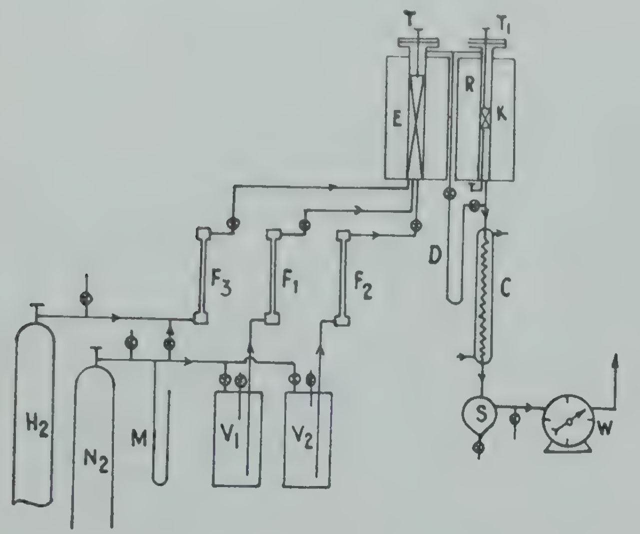


Fig. 1—Flow Diagram of Hydrocarbon Steam Reformation Unit

After reaction in the catalyst bed, the product gas along with excess steam is cooled in the water cooled condenser (C). The condensed water separates out in the separator (S) and the product gas is vented after metering through a wet gasmeter (W). A differential mercury manometer (D) is connected across the reactor to show the pressure drop.

In the actual experiments, the reactor (R) was charged with 25 g. of catalyst of 2 to 3 mm. size. The temperatures of vaporizer and reactor were raised upto 400°C in a current of nitrogen and then water is slowly pushed into the system. While vaporizer temperature was maintained around 400°C, the reactor outlet temperature (T_2) was gradually raised upto 700°C under steam flow which was maintained 75 g./hr. Hydrogen was pushed into the system through the vaporizer at this stage to maintain hydrogen-to-steam ratio of 1:10 by volume for reduction of catalyst. This condition was maintained for about 4 hours to ensure complete reduction and the reactor outlet temperature was raised to 850°C. Heptane was carefully pushed into the system and hydrogen was cut off. The desired temperatures at the reactor outlet was maintained and steam and heptane flows were adjusted to achieve a steam-to-carbon ratio (mole/atom) of 4.0 and the desired liquid hourly space velocity (LHSV) with respect to heptane (g./g. cat/hr). The product gas volume was recorded in the wet gasmeter and the excess steam corresponding to a known volume of gas was estimated from the volume of water collected from the separator in a definite interval of time.

Each catalyst sample was tested for a total period of 65 hours, during which steam-to-carbon molar ratio was kept fixed at 4.0, but the LHSV was varied between 0.6 and 1.0 at a fixed reactor outlet temperature (850°C) and the reactor temperature was varied between 850 and 750°C at a fixed LHSV of 1.0. Under each condition of experiment, product gas sample was collected and analysed several times in an Orsat, to ensure the steady condition. After 58 hours' run, the catalyst bed was steamed at 800°C for about 4 hours to remove carbon deposited on the catalyst, if any, and the experiment was repeated under initial condition of test (LHSV 0.6 and reactor outlet temperature 850°C) to check up whether the initial activity was retained by the catalyst.

Finally, the unit was cooled down under nitrogen flow. The discharged catalyst, after sieving to remove fine dust, was weighed to determine the dusting loss.

The specific surface area of each of the catalyst sample in a reduced condition was determined from nitrogen adsorption isotherm at liquid nitrogen temperature with the help of BET equation.

Results and Discussion

The results of activity tests under various operating conditions, are shown in Table 1 which includes, in addition to product gas composition, the pressure drop across the catalyst bed, hourly volume of the product gas at NTP and the balance of carbon in the feed and product gas on hourly basis. Analysis of the unsaturated component of product gas showed that it consisted mostly of ethylene. So, for convenience, the whole portion of unsaturates in the product gas has been considered as ethylene.

Activity has been defined as the percentage of total carbon in the product gas present as carbon monoxide and carbon dioxide Thus,

$$\text{Activity } (\%) = \frac{(P_{CO}+P_{CO_2})\times 100}{P_{CO}+P_{CO_2}+P_{CH_4}+2P_{C_2H_4}}$$

where P_{CO}, P_{CO_2}, etc. indicate the partial pressures of

TABLE 1—ACTIVITY TEST RESULTS

[Operating pressure—atmospheric; steam-carbon ratio (molar) 4.0]

Cumulative Hours of Run	L.H.S.V., g. heptane g. of cat./hr.	Reactor Temp., °C Inlet	Reactor Temp., °C Outlet	Product Gas Make at N.T.P., Lt/hr.	Press Drop. mm of Hg.	Product Gas Composition, % by vol. CO_2	C_2H_4	CO	H_2	CH_4	Carbon In Feed, g./hr.	Carbon In Product Gas, g./hr.
						Sample NA_1						
7.0	0.6	600	850	77.3	4.0	10.2	Nil	20.2	68.8	0.8	12.6	12.5
20.0	0.8	600	850	101.2	6.0	11.2	Nil	20.0	67.8	1.0	16.8	16.8
25.0	1.0	600	850	123.3	9.0	9.6	Nil	22.2	67.0	1.2	21.0	21.0
37.0	1.0	580	800	110.4	9.0	10.0	1.6	20.8	65.6	2.0	21.0	21.0
47.5	1.0	560	750	105.8	10.0	10.0	1.8	20.0	63.2	5.0	21.0	21.0
50.0	1.0	560	750	101.2	12.0	10.2	2.0	20.4	62.5	5.2	21.0	20.8
56.0	1.0	550	750	101.2	20.0	10.8	1.6	19.2	64.0	4.4	21.0	20.4
58.0	1.0	550	750	98.4	35.0	10.6	1.8	19.8	63.0	4.8	21.0	20.5
65.0	0.6	600	850	74.9	4.0	10.8	Nil	19.8	68.2	1.2	12.6	12.6
						Sample NA_2						
6.0	0.6	600	850	73.0	4.0	11.4	Nil	20.4	67.6	0.6	12.6	12.6
24.0	0.8	600	850	97.9	6.0	10.8	Nil	21.2	67.2	0.8	16.8	16.8
28.0	1.0	600	850	118.4	9.0	10.0	Nil	21.6	67.4	1.0	21.0	20.8
36.0	1.0	580	800	112.1	9.0	10.8	1.2	20.2	66.0	1.8	21.0	21.0
42.0	1.0	550	750	106.8	10.0	13.2	1.2	17.8	65.2	2.6	21.0	20.4
49.0	1.0	550	750	108.6	11.0	12.4	1.2	17.6	66.2	2.6	21.0	20.3
55.0	1.0	550	750	106.8	15.0	12.6	1.4	17.4	66.2	2.4	21.0	20.2
58.0	1.0	550	750	106.8	25.0	12.2	1.2	17.8	66.2	2.6	21.0	20.0
65.0	0.6	600	850	72.0	4.0	11.4	Nil	19.4	68.2	1.0	12.6	12.4
						Sample NA_3						
12.0	0.6	600	850	73.9	4.0	11.8	Nil	19.0	69.0	0.2	12.6	12.3
24.0	0.8	600	850	99.4	6.0	11.6	Nil	19.4	68.6	0.4	16.8	16.7
27.0	1.0	600	850	121.4	9.0	9.0	Nil	21.8	68.0	0.6	21.0	20.8
38.0	1.0	570	800	113.1	10.0	10.8	0.8	20.2	66.8	1.4	21.0	20.8
44.0	1.0	550	750	104.4	10.0	12.4	0.8	18.6	66.4	1.8	21.0	19.6
50.0	1.0	550	750	106.1	11.0	12.8	0.8	19.0	65.6	1.8	21.0	19.8
58.0	1.0	550	750	103.5	21.0	12.6	1.0	19.2	65.4	1.8	21.0	19.6
65.0	0.6	600	850	73.1	4.0	10.6	Nil	20.2	68.6	0.6	12.6	12.3
						Sample NA_4						
6.0	0.6	600	850	74.8	4.0	12.0	Nil	19.8	68.0	0.1	12.6	12.6
24.0	0.8	600	850	98.3	6.0	12.0	Nil	19.6	68.2	0.2	16.8	16.8
30.0	1.0	600	850	123.5	8.0	10.8	Nil	20.0	68.8	0.4	21.0	20.7
35.0	1.0	590	800	113.1	9.0	13.4	0.8	18.6	66.2	1.0	21.0	20.9
46.0	1.0	550	750	108.7	10.0	13.0	0.4	17.8	67.4	1.4	21.0	19.2
52.0	1.0	550	750	109.6	10.0	12.0	0.6	18.8	67.2	1.4	21.0	19.4
58.0	1.0	550	750	104.4	17.0	12.6	0.6	19.2	66.0	1.6	21.0	19.3
65.0	0.6	600	850	73.0	4.0	11.4	Nil	20.2	68.0	0.4	12.6	12.5

(*Contd.*)

Cumulative Hours of Run	L.H.S.V., g. heptane g. of cat./hr.	Reactor Temp., °C		Product Gas Make at N.T.P., Lt/hr.	Press Drop, mm of Hg.	Product Gas Composition, % by vol.					Carbon	
		Inlet	Outlet			CO_2	C_2H_4	CO	H_2	CH_4	In Feed, g./hr.	In Product Gas, g./hr.
						Sample NA_5						
6.0	0.6	600	850	72.2	4.0	10.0	Nil	21.4	68.0	0.6	12.6	12.4
22.0	0.8	600	850	95.7	6.0	11.6	Nil	20.0	67.4	1.0	16.8	16.7
30.0	1.0	600	850	121.8	9.0	10.2	Nil	20.8	67.6	1.4	21.0	21.0
35.0	1.0	580	800	109.6	9.0	11.8	1.2	19.8	65.2	2.0	21.0	21.0
43.0	1.0	580	750	102.7	10.0	12.8	1.6	18.2	64.8	2.6	21.0	20.9
49.0	1.0	550	750	100.9	12.0	13.0	1.4	18.6	64.2	2.8	21.0	19.9
53.0	1.0	550	750	99.2	12.0	12.8	1.6	18.8	64.2	2.6	21.0	19.8
58.0	1.0	550	750	99.2	13.0	13.0	1.6	18.6	64.2	2.6	21.0	19.8
65.0	0.6	600	850	71.3	4.0	11.0	Nil	20.6	67.4	1.0	12.6	12.4
						Sample NA_6						
12.0	0.6	600	850	66.1	4.0	9.0	0.8	22.8	65.2	2.2	12.6	12.5
18.0	0.8	600	850	84.4	6.0	8.8	1.4	22.8	64.4	2.6	16.8	16.7
28.0	1.0	600	850	100.9	9.0	8.0	2.2	23.6	63.2	3.0	21.0	21.0
40.0	1.0	570	800	94.8	10.0	10.8	2.8	21.0	62.0	3.4	21.0	20.7
46.0	1.0	550	750	90.5	10.0	11.2	3.4	20.4	61.0	4.0	21.0	20.5
52.0	1.0	550	750	88.7	10.0	11.0	3.6	20.6	60.6	4.2	21.0	20.4
58.0	1.0	550	750	87.8	11.0	11.4	3.6	20.4	60.2	4.4	21.0	20.4
65.0	0.6	600	850	64.4	4.0	10.0	1.0	21.4	65.0	2.6	12.6	12.5

the respective components in the product gas.

The initial activities of the catalysts at 850°C, 0.6 LHSV and 4.0 steam-to-carbon ratio as well as their activities under same operating condition after 65 hours' run have been shown in Table 2, where the activities at 750°C, 1.0 LHSV and 4.0 steam-to-crabon ratio, are also shown.

TABLE 2—COMPARATIVE ACTIVITIES OF THE CATALYST SAMPLES

Catalyst Sample	Activity at 850°C, 0.6 L.H.S.V. and 4.0 S/C (molar ratio), % reformed		Activity at 750°C, 1.0 L.H.S.V. and 4.0 S/C ratio (molar)
	Initial	After 65 Hours' Run	
NA_1	97.4	96.2	77.7
NA_2	98.1	96.9	86.1
NA_3	99.4	98.1	90.1
NA_4	99.7	98.8	93.3
NA_5	98.1	97.0	84.2
NA_6	89.3	87.2	74.5

The percentage of the feed carbon liberated on the catalyst at LHSV of 1.0 and reactor temperature of 750°C, calculated on the basis of carbon balance data after 58 hours' run (Table 1), is shown in Table 3 along with percentage dusting after 65 hours' run. The specific surface areas of the reduced samples are also shown in Table 3.

Activity and Carbon Liberation: In Fig. 2 activity and carbon liberation corresponding to the different catalyst samples have been plotted against respective percentage of alumina from its basic carbonate ('X').

From curves A and B of Fig. 2, it is clear that initial and final activities (after 65 hours' run) are very close in all cases. This shows that none of the catalyst samples lose any appreciable activity during the period of test. From curve C along with curves A and B, it is observed that the reforming activity first increases with increasing value of 'X' upto somewhere in the region of 40 and then decreases with further increase of 'X' upto 100. Thus, activity of the catalyst increases sequentially from NA_1 to NA_4 and then decreases from NA_4 to NA_6. The γ-alu-

TABLE 3—Carbon Liberation, Dusting and Specific Surface Area of Catalyst Samples

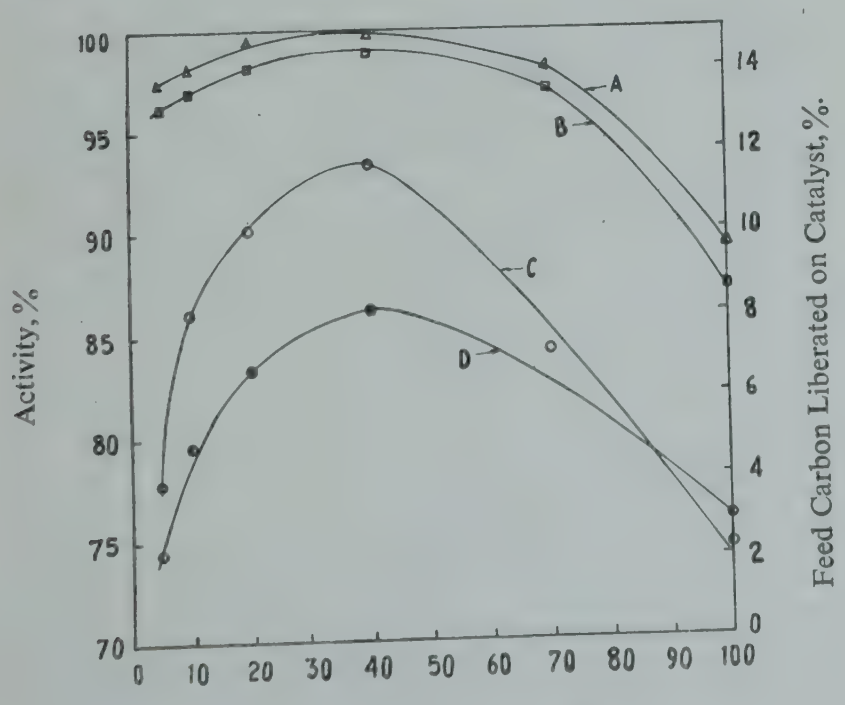
Catalyst Sample	Feed Carbon Liberated on Catalyst*, %	Weight of Catalyst, g.		Dusting of Catalyst, %	Specific Surface area of Discharged Catalysts, m²/g.
		Charged	Discharged (sieved)		
NA_1	2.4	25.0	21.3	14.8	14.1
NA_2	4.8	25.0	22.3	10.8	14.3
NA_3	6.7	25.0	23.0	8.0	19.3
NA_4	8.1	25.0	23.7	5.2	21.6
NA_5	5.2	25.0	24.2	3.2	49.4
NA_6	2.9	25.0	24.6	1.6	56.4

*Operating condition: L.H.S.V. 1.0; S/C 4.0; Temp. 750°C; Hours of run 58.

mina content of the catalysts increases with the value of 'X'[19]. So, it follows that γ-alumina content upto a certain extent has got favourable effect on activity but beyond this optimum limit the effect is reverse.

Specific surface areas of the reduced samples (Table 3) show that surface area increases progressively with increasing concentration of γ-alumina, which was observed also in case of the fresh samples[19]. Thus, in spite of progressive increase in surface area with increasing concentration of γ-alumina, activity decreases after a certain optimum concentration. This is probably due to the fact that distribution of nickel and its size (which play vital role on activity) depend much on the structure of the carrier which changes with the concentration of γ-alumina. However, it requires further investigation to ascertain the reasons for such variation of activity.

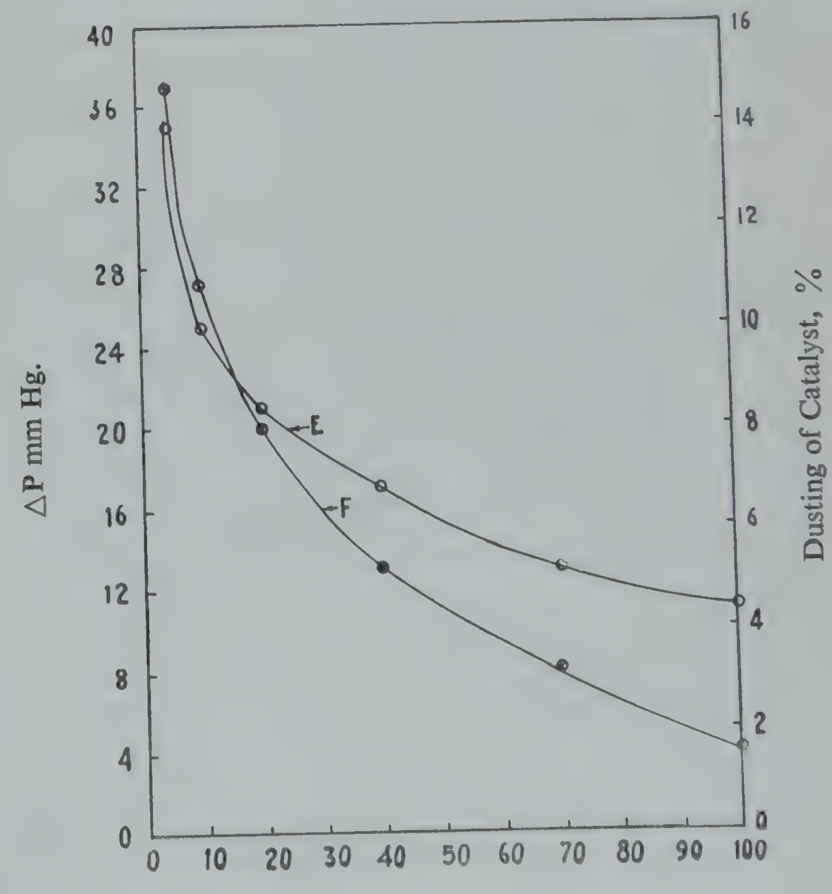
From curve D of Fig. 2, it is interesting to note that the extent of cabon liberation on the catalyst vary in the the same manner as the activity of the catalysts. Thus, the maximum carbon liberation is observed with catalyst NA_4 having the highest activity. More deposition of carbon on the catalyst having the higher reforming acti-



Total Alumina in the Carrier Obtained from its Basic Carbonate, %

Fig. 2—Activity and Carbon Liberation

A. Initial Activity at 850°C and 0.6 LHSV
B. Activity after 65 Hours' Run at 850°C and 0.6 LHSV
C. Activity at 750°C and 1.0 LHSV
D. Per Cent Carbon Liberated at 750°C and 1.0 LHSV



Total Alumina in the Carrier Obtained from its Basic Carbonate, %

Fig. 3—Pressure Drop (△ P) and Dusting

E. Pressure Drop (△ P) across Catalyst Bed after 58 Hours' Run at 750°C. and 1.0 LHSV
F. Percentage Dusting of Catalyst after 65 Hours' Run

vity appears to be due to the fact that higher activity of surface nickel not only increases the rate of reformation, but also the the rate of catalytic cracking of hydrocarbon which is a major reason for carbon liberation.

Stability: Mechanical stability of the samples has been assessed from the loss due to dusting of catalyst and increase in pressure drop across the catalyst bed during the activity tests. Curve E of Fig. 3 as well as Table 3 show that dusting characteristics decrease with increasing value of 'X'. An increase in the pressure drop during activity test upto 58 hours' run, shows a similar relationship (Curve F of Fig. 3). So, both dusting of catalyst and rise of pressure drop across the catalyst bed decrease continuously from NA_1 to NA_6, i.e. with increasing concentration of γ-alumina. So, it follows that the presence of γ-alumina increases the stability of a catalyst. This is contrary to the view that γ-alumina cannot make a stable carrier due to phase transformation to the α-form resulting in collapse of the structure[5]. In fact, the results of the present investigation show that presence of γ-alumina in the carrier is preferable from the stability point of view. Higher mechanical stability of nickel catalyst with γ-alumina as carrier, is also reported by Moehl[3]. The fact that initial mechanical strength of catalyst containing γ-alumina is higher[19,21] and that the structural transformation of the γ-alumina under reaction condition is inhibited in presence of nickel[20], appear to be responsible for higher stability with more γ-alumina content.

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The isothermal relationship between surface area and time of sintering $dA/dt = -Ks (A-Af)$ has been applied to demonstrate the relationship between changes in surface area and temperature of sintering. A procedure for calculation of approximate activation energy of such changes from surface area measurements at different temperatures has been proposed and activation energies for nickel oxide, alumina, ferric oxide and ferric oxide-chromium oxide are obtained as 10.0, 6.0, 6.5 and 3.8 K Cal/mole respectively in the temperature range 673 to 1273°K.

Relationship Between Surface Area and Temperature of Sintering in NiO, Al_2O_3, Fe_2O_3 & Fe_2O_3-Cr_2O_3 System

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Introduction

The heat treatment of solids, particularly of the oxides used as catalyst or catalyst support, has wide applicability in imparting the desired mechanical strength and specificity to the catalysts. Heat treatment is associated with the term sintering. This term is generally used to express the conditions at elevated temperatures, when the crystallites or atoms of a substance grow together resulting in the formation of bigger crystallites. The process tends to decrease the specific surface area, porosity and an increase in particle size and density of solid.

The factors causing the increase and decrease in surface area during isothermal decomposition of solids have been reviewed by Nicholson[1]. Theoretical models for sintering[2–3] are highly idealized and are difficult to present in terms of surface area. Sintering has been considered a process involving an energy barrier, so that the rate is a function of both time and temperature. The different rate expressions[4–8] for sintering in relation with variation in grain size, pore diameter, density and surface area, etc. are based on the studies at a constant temperature and varying time. Much less attention has been paid towards the study of sintering rates as a function of temperature. Ramseier[9] has presented results of study of sintering process and has shown that the rate constant as a function of temperature can be satisfactorily represented by an exponential equation.

The decrease in surface area on sintering is believed to occur due to the movement of ions of the solid along the surface of the crystallite (surface diffusion) resulting in filling up of the surface irregularities as well as cracks between the neighbouring crystallites, thus cementing the crystallites together. Another mechanism which may have its contribution towards reduction in the surface area on heating is the collapsing or shrinkage of pores. The investigation has been carried out with four samples comprising nickel oxide, alumina, ferric oxide, ferric oxide-chromium oxide in four series. Each series consisted of 5 to 9 samples sintered in the range 673 to 1273°K. In case of alumina samples which contained quite an appreciable amount of combined water (8.3 per cent as determined in our sample compared to 2.8 and 3.1 per cent respectively in NiO and Fe_2O_3), the decrease in surface area may well be due to the collapsing of finer pores during evolution of this combined water. Thus, any attempt to determine the activation energy of sintering for such porous solids, e.g. alumina, from surface area measurement may not lead to the true activation energy of sintering of refractory oxide alumina. The present work deals with the nature of dependence of surface area on temperature of sintering. Attempt has been made to present a working procedure for evaluation of energy of activation of sintering process.

Experimental

Preparation of Samlpes

(1) *Nickel Oxide* (NiO). To a solution of nickel nitrate (AnalaR), ammonium carbonate solution was added.

The precipitate was washed, dried and heated at different temperatures between 400 and 1000°C for 2 hours each.

(2) *Alumina* (Al_2O_3): This was also precipitated from aluminium nitrate with ammonium carbonate solution. The precipitate was washed, dried and heated at different temperatures between 400-1000°C for 2 hours each.

(3) *Ferric Oxide* (Fe_2O_3): Hydrated iron oxide was obtained by precipitation from ferrous sulphate and ammonium carbonate. The precipitate was washed, dried and samples were prepared similarly as in NiO and Al_2O_3.

(4) *Ferric Oxide-Chromium Oxide* (Fe_2O_3-Cr_2O_3): The dried precipitate as obtained in (3), was mixed with the requisite amount of chromic acid (to give 7 per cent chromium in the finished samples) and thoroughly kneaded. The samples were prepared by heating at different temperatures as above.

Measurements

Surface area determinations of samples sintered at different temperatures were carried out by the usual BET method using nitrogen as adsorbate.

Results and Discussion

Surface Area and Mechanism of Sintering: The kinetics and mechanism of sintering is greatly influenced by temperature, and for comparison of different substances the ratio α which is equal to T/Tm—where T and Tm are temperatures of sintering and melting respectively of the substance is generally taken into consideration. Gregg[10] and Huttig[11] have classified sintering into the following three processes depending upon the value of α (1) adhesion, (2) surface diffusion and (3) lattice or bulk diffusion. Adhesion occurs only at lower temperature and Nicholson[1] has pointed out that when α is less than 0.2, adhesion is the main mechanism of sintering. From 0.2 to 0.35 α surface diffusion is the mechanism and bulk diffusion is operative only above the Tammann temperature (α=0.5). It is to be expected that either of these three sintering mechanisms will have a different effect on the rate and extent of change in surface area.

The change in surface area in the temperature range under investigation has been plotted (Fig. 1), while Fig. 2 gives the plot of surface area against α. Surface diffusion or bulk diffusion is expected to be the mechanism of sintering in the temperature range under consideration. In the case of nickel oxide, a sharp break in the curve (Fig. 2) is observed at $\alpha = 0.35$, which may suggest that sintering might be occurring by two processes, and about 800-820°K the change-over from one process to another might be taking place. In alumina there is a steady decrease in surface area and only above $\alpha = 0.5$ there is a little tendency for the curve to take a turn which may represent the beginning of another sintering mechanism at

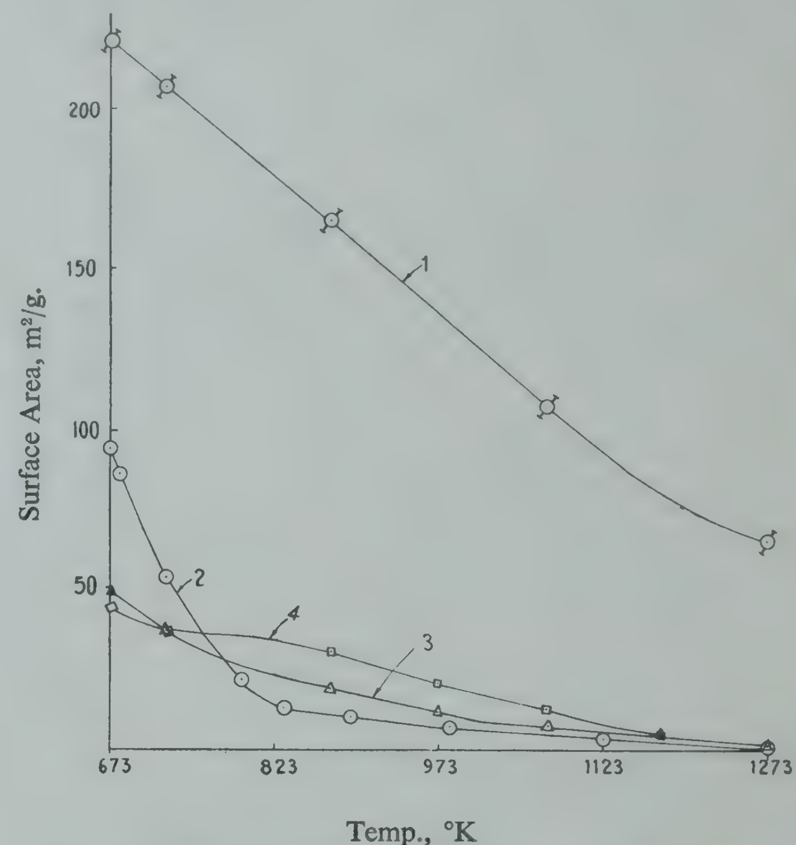


Fig. 1—Relation between Surface Area and Temperature
1. Alumina 2. Nickel Oxide 3. Ferric Oxide
4. Ferric Oxide-Chromic Oxide

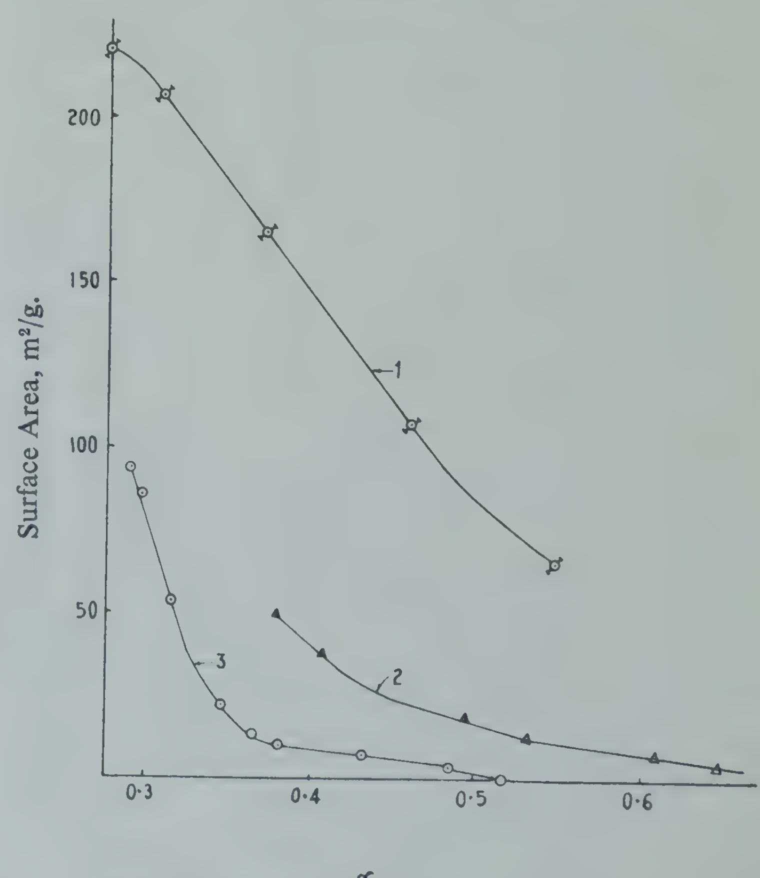


Fig. 2—Relationship between Surface Area and ∝ (T/Tm)
1. Alumina 2. Ferric Oxide 3. Nickel Oxide

about 1120-1140°K. The sintering process in ferric oxide and ferric oxide-chromium oxide appears to be more or less similar to that in the case of alumina, and from surface area curves it can be assumed that one type of sintering mechanism is predominant upto 950°K and above this another mechanism may be operating.

Relationship between Surface Area and Temperature: For the relationship between sintering and changes in physical parameters, various isothermal rate expressions have been put forward which give relationships between the time of sintering at constant temperature and grain size[5], pore volume[6], pore diameter[6,8] and surface area[1,7].

Among the various relationships on sintering rate and surface area, the following one, given by Nicholson[1], is the simplest:

$$\frac{dA}{dt} = -\,Ks\,(A-Af),$$

where Ks = (Rate) constant,
A = initial surface area,
Af = surface area finally attained
and t = time of sintering.

The validity of the above equation has been tested by the present authors by plotting Log (A−Af) against t which should yield a straight line with a slope giving Ks, the value of which will depend on the temperature of sintering. Nicholson[1] has obtained results confirming to this relationship and has particularly mentioned that this relationship should be expected to apply at least in the region where surface diffusion is predominant.

The use of the above equation could be made considering time as constant and varying the temperature of sintering, T. The equation can be rewritten as $\frac{dS}{dT} = -K\,(Si-Sf)$, where Si = initial surface area at T°K, Sf = final surface area attained at highest temp. of sintering under consideration, T = temperature of sintering, °K and K = a constant which may be called as sintering coefficient representing a change in surface area due to sintering/unit change in surface area degree °K.

If the above equation holds good, a plot of Log (Si−Sf) against T should also give a straight line. Fig. 3 gives the plot of Log (Si−Sf) against T, and in fact a straight line has been obtained in all the four oxides under investigation. This indicates that surface area bears a similar relationship with temperature as with time.

Procedure for calculation of Activation Energy: Since the sintering coefficient is a function of both time as well as temperature, and if the values of K can be obtained at different temperatures, Arrhenius equation can be used to calculate the apparent activation energy.

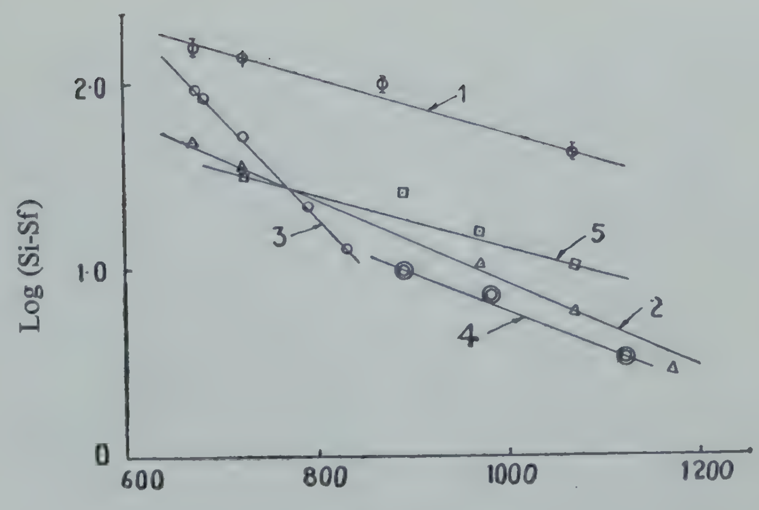
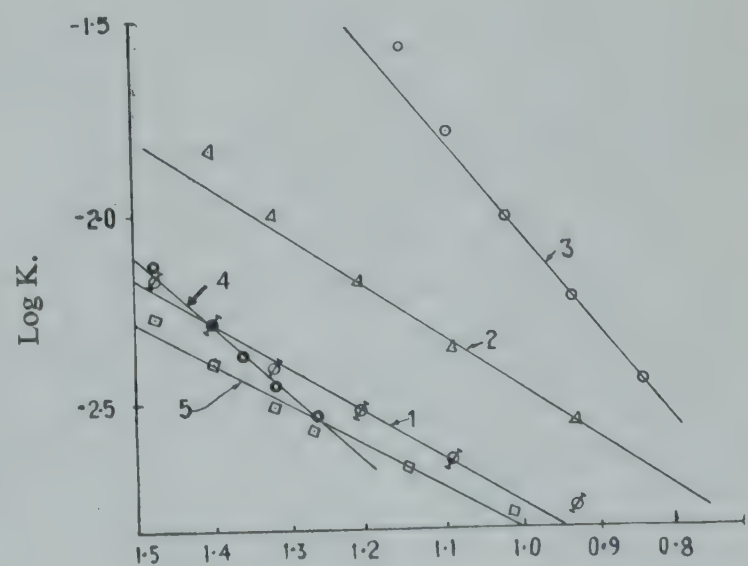


Fig. 3—Plot of Log (Si-Sf) against Temperature
1. Alumina 2. Ferric Oxide 3. Nickel Oxide 673-833°K
4. Nickel Oxide 833-1125°K 5. Ferric Oxide-Chromium Oxide

The numerical value of K averaged over entire temperature range was calculated from the slope of the straight line obtained by plotting Log (Si−Sf) against T. Substituting this value of K in equation $\frac{dS}{dT} = -K(Si-Sf)$, $\frac{dS}{dT}$ can be calculated for the entire range of change in the observed surface area (Si−Sf). Employing these calculated values of $\frac{dS}{dT}$, values of K at different temperatures have been obtained taking the values of (Si−Sf) at corresponding temperatures.

Fig. 4 shows the plots of Log K against 1/T and it can



$\frac{1}{T} \times 10^3$

Fig. 4—Arrhenius Plot for Activation Energy Calculation
1. Alumina 2. Ferric Oxide 3. Nickel Oxide 673-833°K
4. Nickel Oxide 833-1123 °K 5. Ferric Oxide-Chromic Oxide

be seen that straight lines are obtained for all the oxides. The values of apparent activation energy of sintering can thus be calculated from the slopes of these lines.

Nickel Oxide: Since a sharp change in the rate of decrease in surface area was observed in the plot of surface area against temperature (Fig. 2), it was considered that two different mechanisms of sintering may be operating. The entire range of temperature has been split up in two, viz. 673-833 and 833-1123°K, and the straight lines for Arrhenius plot have been obtained separately. The activation energy calculated comes out to be 10.0 and 11.5 K.Cal/mole respectively. Tyoichiro Moriyama[12] has obtained values of activation energy of sintering for NiO in the range of 6.8-8.6 while Tatsuya Imoto[13] has obtained 13.0 K.Cal/mole, which compare well with our results.

Alumina: The precipitated form of alumina gel when heated to 400°C may contain a mixture of γA1.O.OH and anhydrous alumina, probably k-alumina. By a somewhat complex series of polymorphic changes, the k-alumina decomposes over the range 400-1000°C to give ultimately α-alumina. The activation energy of sintering of alumina above 1000°C is in the order of 130-150 K.Cal/mole. The value obtained by our method in the range of 400-1000°C is about 6.0 K.Cal/mole. Such a large discrepancy, as explained earlier, may be due to the fact that in the temperature range of 400-1000°C alumina undergoes several complex changes besides sintering, the details of which are not yet clear, and any value for the activation energy in this temperature range may not represent the true activation energy of sintering as in refractory Al_2O_3 above 1000°C.

Ferric Oxide and Ferric Oxide-Chromium Oxide: Since the values in literature for ferric oxide and ferric oxide-chromium oxide for the activation energy of sintering in the range 400-900°C could not be obtained, a comparison cannot be made with the values 6.5 and 3.8 k.cal/mole respectively obtained by our method.

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The catalytic activity of ferric oxide-chromium oxide and copper oxide-zinc oxide types of commercial shift conversion catalysts has been studied in the laboratory and their activation energy found from the Arrhenius plot which was obtained by least square technique. The various factors influencing the performance of the catalyst, such as size, operating pressure, diffusion restrictions in small pores, effect of aging or sintering have been studied in the context of design considerations. The basic approach to the design of adiabatic shift converters has been discussed and as a case study, temperature and conversion profiles of an arbitrary converter for use with both types of catalysts have been illustrated.

An Approach to the Design of Shift Converter from Laboratory Data

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Introduction

The catalytic conversion of carbon monoxide with steam ($CO+H_2O \rightarrow CO_2+H_2+Q$), commonly known as water gas shift reaction finds wide application in fertilizer and allied industries. Now-a-days, commercially a combination of two types of catalysts are used. One is the conventional H. T. catalyst (Fe_2O_3-Cr_2O_3 type) which works efficiently in the range 350-500°C and the other the L.T. catalyst (with copper as active component) which while utilizing the advantage of better equilibrium conversion at lower temperatures, catalyses the reaction efficiently in the range 190-270°C.

From the process design point of view, the principal object is to estimate the optimum catalyst volume which will give a guaranteed performance in a commercial unit for a certain specified period, usually extending to 2-3 years.

A survey of literature[1–13] reveals that various forms of empirical rate equations have been suggested by different authors for the conversion reaction. The application[12–13] of most of these rate equations, for checking the catalyst volumes in some industrial converters shows that the volume in actual use is usually more than the calculated volume. In reality, even with this extra volume the guaranteed performance is seldom obtained throughout the specified period of run.

In the present investigation, attempts have been made to ascertain the factors responsible for such discrepancies. The present work also aims at seeking a logical approach, on the basis of laboratory data, for calculating catalyst volumes required in the commercial converters which may be operated under preset conditions to give the desired conversion for a specific period of run.

The approach is based on an expression of catalytic activities in terms of an equation valid for the second order reaction, followed by modification of the rate constant values by accounting for factors, such as size of the catalyst, diffusion restriction in pores, operating pressure, temperatures and period of run, which may cause changes in the catalytic efficiency in commercial reactors. The design procedure by utilizing the modified rate constant values has been illustrated for an arbitrary reactor.

While considering the application of a rate equation obtained on the basis of laboratory data for estimation of catalyst volume required for commercial converters, it is necessary to examine the nature of laboratory test *vis-a-vis* the conditions of industrial operation. For obtaining empirical form of rate equations, the laboratory tests are usually conducted with smaller size of catalyst, to keep the reaction in the kinetic zone. Besides, experiments are often conducted at atmospheric pressure, whereas commercial units are advantageously run at 10 to 30 atmospheres pressure. The effect of catalyst size and operating pressure on apparent reaction rate has been studied [3,14–17] widely but little information is avail-

able on the effect of temperature and period of run on the observed rate constants. The effect of temperature on catalyst texture has been shown in an earlier investigation[18]. If the catalyst undergoes such changes in texture at a very slow rate during operation, the extent of such changes may not affect the catalytic efficiency in the laboratory testing unit to any measurable extent. But the situation may be different for commercial units where the cumulative effect of such changes may bring about appreciable deterioration in catalyst activity during prolonged operations.

Before formulating a suitable form of rate equation, it is considered worthwhile to examine some of the well-known equations. Laupichler[1], Atwood[3] and Mars[8] assumed the rate to be first order with respect to carbon monoxide. But according to Moe[16], the rate varies with partial pressure of water vapour. Hence, whether the observed data can be represented by means of a rate expression valid for first order reaction remains controversial.

Both Bortolini[6] and Laupichler[1] considered the reaction rate controlled by external diffusion. But it was later observed by Wicke[19] and others[8,20] that it is controlled mainly by internal diffusion in the catalyst pores.

Kulkova and Temkin[2] observed that hydrogen in the feed gas has a retarding effect on the rate of forward reaction, but carbon dioxide has no such effect. Different views are, however, expressed by other investigators,[8,21] according to whom the retarding effect of carbon dioxide is quite significant.

Bohlbro[9] proposed an exponential type rate equation, the exponents of which were found to vary within certain ranges of temperature. Unlike Temkin and Kulkova, he observed that hydrogen has no retarding effect. However, indications have been obtained in this laboratory that hydrogen above a certain partial pressure does impart a retarding effect on the reaction rate (unpublished work —S. P. Sen, B. Sen and S. K. Singh).

From the above consideration it can be said that an appropriate rate equation will be one which can interpret and explain all observed data. As will be shown subsequently, a modified rate expression valid for the second order reversible reaction, as given below, is adequate.

Representing mole number of carbon monoxide, water, carbon dioxide, hydrogen and inerts, the usual constituents of the feed gas in one mole of inlet gas by m, n, p, q and (1-m-n-p-q) respectively and the degree of conversion by x,

the rate of forward reaction is

$$\frac{dx}{dt} = r_f = k\,(m-mx)\,(n-mx)$$

and the rate of backward reaction is

$$\frac{dx}{dt} = r_b = k'\,(p+mx)\,(q+mx)$$

∴ The overall rate of the reaction—

$$r = k\,(m-mx)\,(n-mx) - k'\,(p+mx)\,(q+mx)$$

$$= k\left[(m-mx)(n-mx) - \frac{(p+mx)(q+mx)}{K}\right] \quad (1)$$

where k and k′ = rate constants for the forward and backward reaction, and K = equilibrium constant for water gas shift reaction.

Experimental

The investigations were carried out with two types of commercially available shift catalysts—ferric oxide-chromium oxide and copper oxide-zinc oxide. The original samples were in the form of cylindrical tablets of 6×6 mm. size which were crushed and sieved to obtain the desired sizes. For determination of activation energy, measurements at different temperatures were carried out with 1.2-1.7 mm. granules. The original tablets were used for studying the effect of pressure and change of activity with time. The activity measurements were carried out in an apparatus described earlier[22]. A feed gas having the following composition (per cent on dry basis) was used in all the experiments: carbon dioxide 16.5-18.5, carbon monoxide 4.5-7.5, hydrogen 57.5-60 and inerts rest.

Surface area, pore volume and pore size distribution of the reduced samples were determined by methods described earlier[23]. In the present work, however, for better assessment of smaller pores, a porosimeter* of higher working pressure range (15,000 psi) was used.

Results and Discussion

Arrhenius relationship of rate constant with temperature are shown in Figs. 1 and 2. These were obtained by application of least square technique[24]. The energy of activation for the two catalysts from the plots are 7.2 and 3.5 Kcal/mole. respectively. The activation energies were evaluated in order to get an idea as to how these values compare with those found by different workers. For both the catalysts, widely divergent values have been reported in the literature [25–28] ranging from 4 to 27 K.cal/mole. The large differences in activation energies may be

* Aminco Model No. 5—7121 Sp.

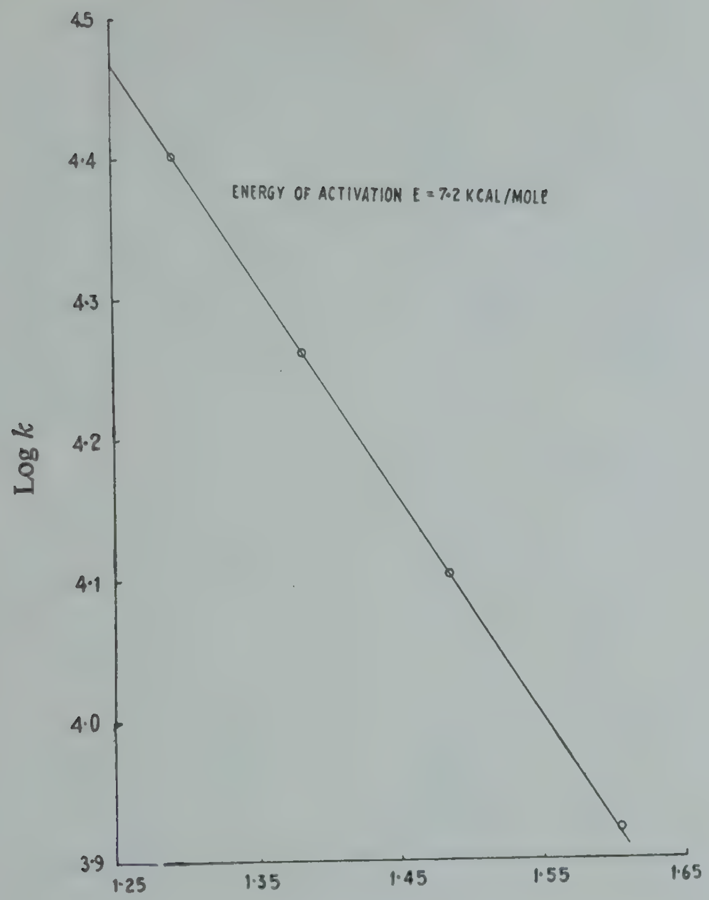


Fig. 1—Variation of Rate Constant with Temperature for H. T. Catalyst

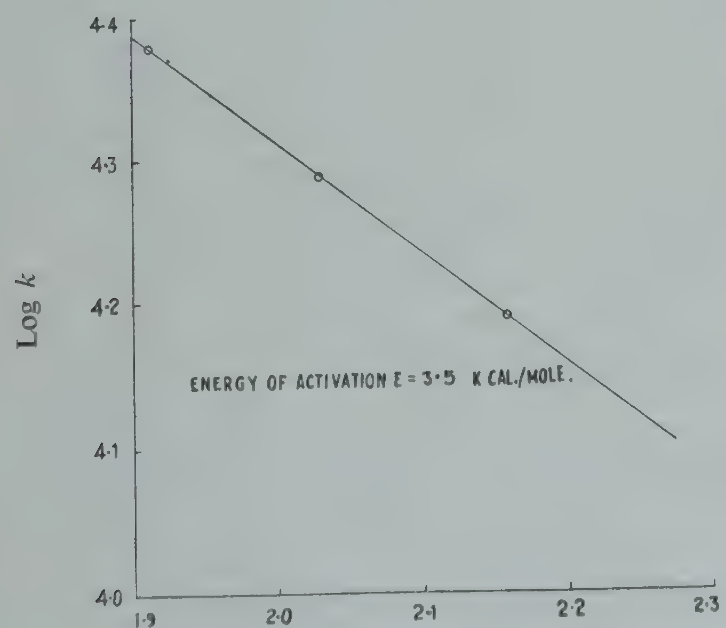


Fig. 2—Variation of Rate Constant with Temperature for L. T. Catalyst

due to differences in pellet size and specific surface area rather than to difference in intrinsic activity as pointed out by Ruthven[17].

Now it is to be seen how equation 1 developed and used for calculating the rate constants can be modified to accommodate the factors which may cause progressive changes in overall efficiency of the catalyst in industrial units.

It has already been pointed out that the size of the catalyst and the operating pressure are the two factors which affect the observed rate constants and which can be conveniently determined. In previous publications[23,29] the effects of size and operating pressure on the activity of the catalyst have been discussed. The experimentally determined effectiveness factors (at 400 and 220°C respectively and atmospheric pressure) for different sizes of the two catalysts as well as calculated values, following Wheeler's[30] concept as communicated earlier[23], is presented in Table 1. It can be seen that the experimental

TABLE 1—EFFECTIVENESS FACTOR OF H.T. AND L.T. CATALYSTS

Size Range, mm.	H.T. Catalyst		L.T. Catalyst	
	$E_{exp.}$	$E_{Wheeler}$	$E_{exp.}$	$E_{Wheeler}$
0.4-0.52	0.998	1.0	0.996	1.00
0.9-1.3	0.962	0.975	0.960	0.971
1.2-1.7	0.920	0.923	0.900	0.921
2.0-2.2	0.882	0.891	0.863	0.873
4.8-5.3	0.802	0.814	0.789	0.791
6×6 Tablets	0.778	0.782	0.737	0.742

and calculated values are quite close. Instead of calculating the effectiveness factors on the basis of average pore radius, as is usually done, the entire pore size distribution range of the catalysts was considered for calculations. The surface area, pore volume and pore size distribution of the two types of catalysts are given in Table 2.

The effects of pressure on 6×6 mm. size tablets for both the types of catalysts are given in Table 3. The activity factor (Table 3) is the ratio $\frac{k_p}{k_A}$ where k_p and k_A are the apparent rate constants at p atmosphere and one atmosphere respectively, calculated from experimental results by using equation 1.

As mentioned earlier, the principal factors which may cause deterioration in the activity of the shift catalyst are temperature and time of operation. These two factors lower the surface area and bring about changes in the pore size distribution[31,32]. Besides surface area directly affecting the catalyst activity, the change in pore size distribution will modify the effect of pressure. But there appears to be no simple relationship[31] between catalyst activity and these factors. It is rather difficult to indi-

TABLE 2—Surface Area, Porosity and Pore Size Distribution of H. T. and L. T. Catalysts (Reduced)

Catalyst	Surface	Porosity		Pore Size Distribution, % by volume						
	Area, m^2/g.	cc./g.	cc./100cc.	4-60 Å	60-100 Å	100-175 Å	175-300 Å	300-400 Å	400-500 Å	500-75000 Å
H.T.	23.7	0.1988	48.6	5.2	14.3	23.9	25.7	9.0	5.4	16.5
L.T.	27.6	0.243	58.8	16.5	6.8	55.6	12.8	1.4	0.9	6.0

TABLE 3—Effect of Pressure on 6×6 mm Tablets

Pressure, Atm.,	H. T. Catalyst		L. T. Catalyst	
	Apparent Rate Constant at 400°C., NM^3/hr/M^3	Activity Factor, $\frac{k_p}{k_A}$	Apparent Rate Constant at 220°C., NM^3/hr/M^3	Activity Factor, $\frac{k_p}{k_A}$
1	9800	1.0	14320	1.0
6	14500	1.48	25800	1.8
12	25400	2.60	38700	2.7

vidually assess these factors and correlate them with efficiency of catalyst.

In view of this, attempts have been made to assess the combined effect of time and reaction temperature on the activity of the catalyst. The effect of days on stream on the initial activity for the two catalysts are given in Figs. 3 and 4. In Fig. 3 one plot is for the laboratory data obtained after a continuous run for 30 days (720 hours) and the other is actually computed from the data of a commercial reactor operating at the following inlet and outlet temperatures respectively (350-380 and 380-410°C). It can be seen that the initial rate of change in activity is small and as such if a test run for evaluation of activity is continued for 2 to 3 days the magnitude of the change cannot be correctly ascertained. Keeping this specific point in view, the test run was continued till change in activity is measurable with fair degree of accuracy. In this way 30 days' run in the laboratory was found necessary to detect such changes in activity. The extrapolated values of laboratory data are quite in agreement with those computed

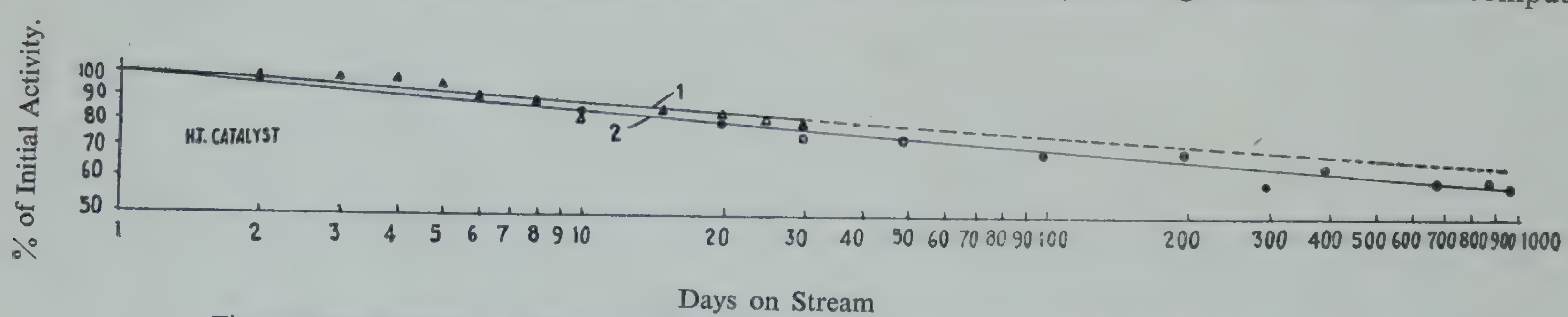


Fig. 3—Effect of Days on Stream on Initial Activity 1. Laboratory Data at 400°C, 2. Plant Data

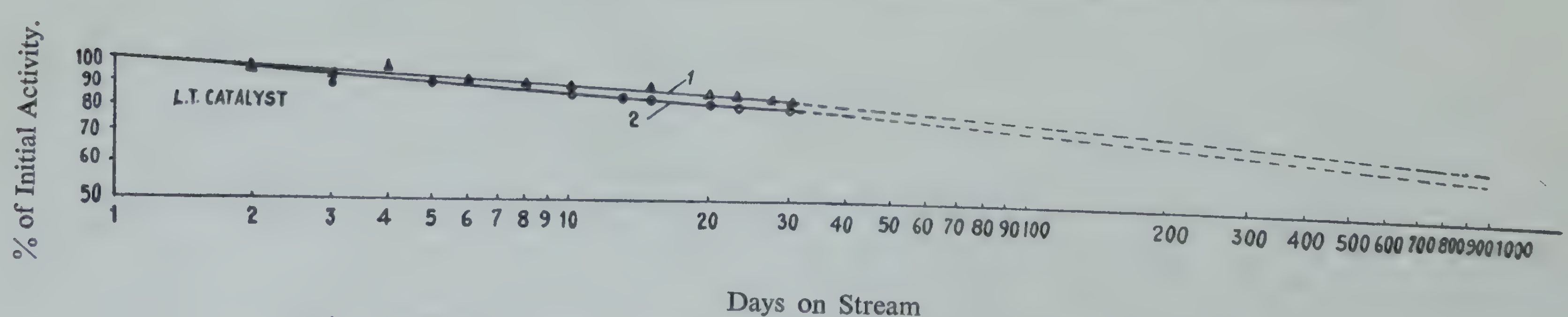


Fig. 4—Effect of Days on Stream on Initial Activity 1. At 190°C, 2. At 220°C

from the commercial reactor. For design calculations the latter values have been used to allow a reasonable margin.

The basic principles by which the catalyst volume in catalytic converters can be estimated from measured reaction rates may be briefly outlined as follows.

From heat balance the adiabatic temperature rise across the catalyst bed can be expressed as

$$dt = \frac{Y \times \Delta H}{FC_p} dx \qquad (2)$$

where Y = Concentration of CO in the feed gas, moles

F = Total feed rate, moles/hr.

C_p = Average mean specific heat for the feed gas, cal/mole.

ΔH = Heat of reaction, cal/mole.

For practical purposes, ΔH and C_p may be taken to be constant for fixed feed gas composition and over the reaction temperature range, because of the very small changes of these values with temperature. Equation 2 can be written in the form $dt = \alpha\, dx$, which when intergrated between the limits T_o and T becomes

$$T = T_o + \alpha \Delta x \qquad (3)$$

where T_o = Inlet temperature

T = Temperature at conversion Δx and

$$\alpha = \frac{Y \times \Delta H}{FC_p} = \text{Constant.}$$

Again from material balance across the catalyst bed

$$f\, dx = r\, dV \qquad (4)$$

where f = flow rate of carbon monoxide, NM^3/hr

r = reaction rate, NM^3 of CO-converted/hr/M^3 of catalyst

dV = elemental catalyst volume corresponding to a conversion of dx.

By changing equation 4 into a differential form

$$\Delta V = \frac{1}{r} \times f \times \Delta x \qquad (5)$$

From the energy balance

$$Y dx = r \times Ac \times dz \qquad (6)$$

$$\text{or } dz = \frac{Y}{r \times Ac} dx = R\, dx \qquad (7)$$

where $R = \dfrac{Y}{r \times Ac}$

Ac = cross sectional area of catalyst bed,

dz = incremental catalyst bed height.

For an increment of Δx conversion

$$\Delta Z = R_{av} \times \Delta x \qquad (8)$$

where R_{av} = average value of R

The catalyst volume and bed height required for increments of Δx conversion can be calculated from equations 5 and 8 by stepwise calculation.

The above procedure forms the basis of the present design calculation. In the stepwise calculations by the above procedure, it is needless to mention that smaller the value of Δx chosen, the less is the calculation error. At temperatures where the conversion approaches equilibrium values, it is desirable to choose smaller incremental conversions because of the abrupt lowering of the reaction rates. Otherwise, much lower catalyst volumes will be obtained from calculations than actually required. This has been given due consideration as can be seen from Tables 4 and 5.

It is worthwhile to examine how the data obtained in the laboratory can be suitably utilized with the help of the above design procedure for estimating catalyst volume of an industrial converter.

TABLE 4—Reaction Rate, Temperature and Conversion Profile with H.T. Catalyst

Reaction Rate (r), $NM^3/hr/M^3$	Conversion	Temperature, °C	Catalyst Bed Depth, M	Catalyst Volume, M^3
120	0	350	0	0
90	0.20	359.3	0.650	1.07
56.1	0.40	368.6	1.612	2.66
31.93	0.50	373.2	3.248	5.36
13.5	0.60	377.8	6.763	11.19

TABLE 5—Reaction Rate, Temperature and Conversion Profile With L.T. Catalyst

Reaction Rate (r), $NM^3/hr/M^3$	Conversion	Temperature, °C	Catalyst Bed Depth, M.	Catalyst Volume, M^3
246	0	200	0	0
204	0.20	209.3	0.2415	0.398
157.2	0.40	218.6	0.5445	0.895
103.1	0.6	228	0.9785	1.615
45.0	0.80	237.3	1.8385	3.03
13.94	0.90	241.8	3.1005	5.11

As a case study, the following feed gas and operating conditions were considered**.

Feed gas	Feed, Nm^3/hr	Volume, % Wet	Dry
CO_2	1922	13.00	22.05
CO	550	3.95	6.31
H_2	5356	38.50	61.50
H_2O	5222	37.50	—
Inerts	875	6.25	10.14
Total	13925	100.00	100.00

The process conditions considered are

Inlet temperature = 350°C for H.T. catalyst and 200°C for L.T. catalyst,

Operating pressure = 12 atm.

Catalyst size = 6×6 mm. tablets

Period of run = 2 years

The main purpose is to illustrate the procedure for estimating the optimum catalyst volume for industrial converters. Hence, instead of considering a specific conversion, catalyst volumes were estimated in a stepwise manner for different incremental conversions and the temperature and conversion profiles plotted accordingly.

For the temperature range 200-400°C on the basis of the average gas composition, the calculated values[33] of the average mean specific heat and heat of reaction are: $C_p = 8.04$ Cal/mole and $\triangle H = 9444$ Cal/mole and

$$\alpha \text{ of equn. } 3 = \frac{Y \triangle H}{FC_p} = \frac{550 \times 9444}{13925 \times 8.04} = 46.4 \qquad (9)$$

Now the value of α being known, the bed temperature after any specific conversion can be calculated from equation 3.

In consideration of the points discussed, the rate constant of equation 1 can be modified in the following manner to give the design rate constant k_d.

$$k_d = k \times a \times b \times c \qquad (10)$$

where a = factor for diffusional resistance of the pores (effectiveness factor)

b = aging factor (loss of original activity due to time on stream)

c = Pressure factor (increase in activity due to increase of pressure).

The use of the design rate constant values, which may be evaluated from equation 10, is illustrated below for H.T. catalyst.

Under the specified operating conditions for our case study the factors a, b, c of equation 10 are: $a = 0.778$ (from Table 1), $b = 0.585$ (from Fig. 3) and $c = 2.60$ (from Table 3).

Substituting these values in equation 10, we get

$$k_d = k \times 1.19 \qquad (11)$$

The adiabatic temperature rise for an increment of 20 per cent conversion with respect to an inlet temperature 350°C can be calculated from equations 3 and 9.

$$T_1 = 350 + 46.4 \times 0.20 = 359.3°C$$

Now the reaction rate of 350°C (x=0) computed from Fig. 1 and equations 1 and 11 is as follows:

$$r_{350} = 8279 \times 1.19 \left(0.01481 - \frac{0.0531}{20.3}\right) = 120$$

Similarly, the rate at 359.3°C ($x = 0.20$), viz. $r_{359\cdot3}$

$$= 8954 \times 1.19 \left(0.01155 - \frac{0.0572}{18.156}\right) = 90$$

and the values of R of equation 7 in the present case are

$$R_{350} = \frac{Y}{r_{350} \times Ac} = \frac{550}{120 \times 1.65} = 2.78 \text{ and}$$

$$R_{359\cdot3} = \frac{550}{90 \times 1.65} = 3.71$$

Now, from equation 8 the bed depth required for the 1st increment of 20% conversion is as follows:

$$\triangle Z_1 = \frac{2.78 + 3.71}{2} \times 0.20 = 0.650 \text{ m}$$

and the corresponding volume

$$\triangle V_1 = 0.650 \times 1.65 = 1.07 \text{ m}^3.$$

Proceeding in the same manner, the bed depth required for the next increment of 20% conversion

$$\triangle Z_2 = \frac{3.71 + 5.95}{2} \times 0.2 = 0.962 \text{ m}$$

$$\text{and } \triangle V_2 = 0.962 \times 1.65 = 0.587 \text{ m}^3$$

or for a total conversion of 40 per cent, the catalyst bed height and volume are 1.612 meters and 2.66 m^3 respectively.

The results of further calculations for H.T. catalyst are

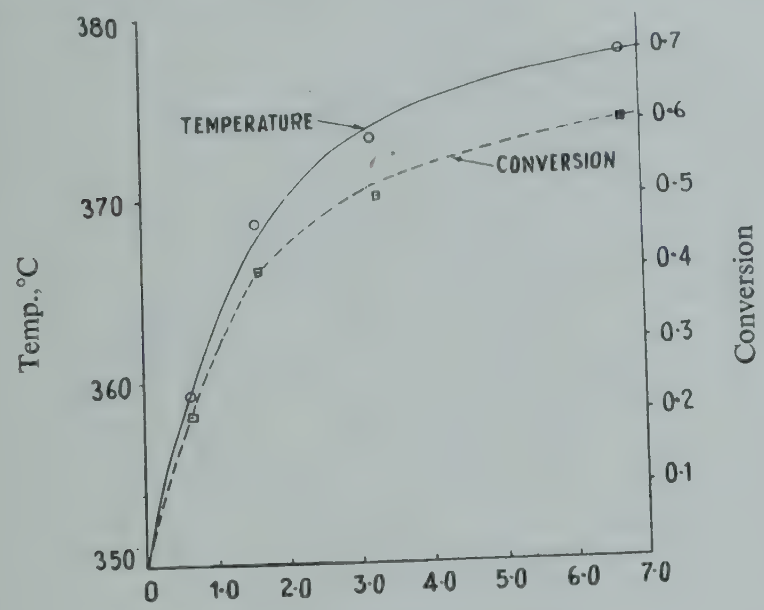
**The feed gas composition considered for our case study is similar to that of a commercial reactor after 1st stage of conversion using H. T. catalyst operating at a pressure of 12 atmosphere. The cross sectional area of the converter = 1.65 m^2.

shown in Table 4 and the temperature and conversion profiles are shown in Fig. 5.

Applying the above procedure for the L.T. catalyst the values of a, b and c of equation 10 from Table 1, Fig. 4 and Table 3 are 0.737, 0.625 and 2.7 respectively and the design rate constant k_d can be expressed as

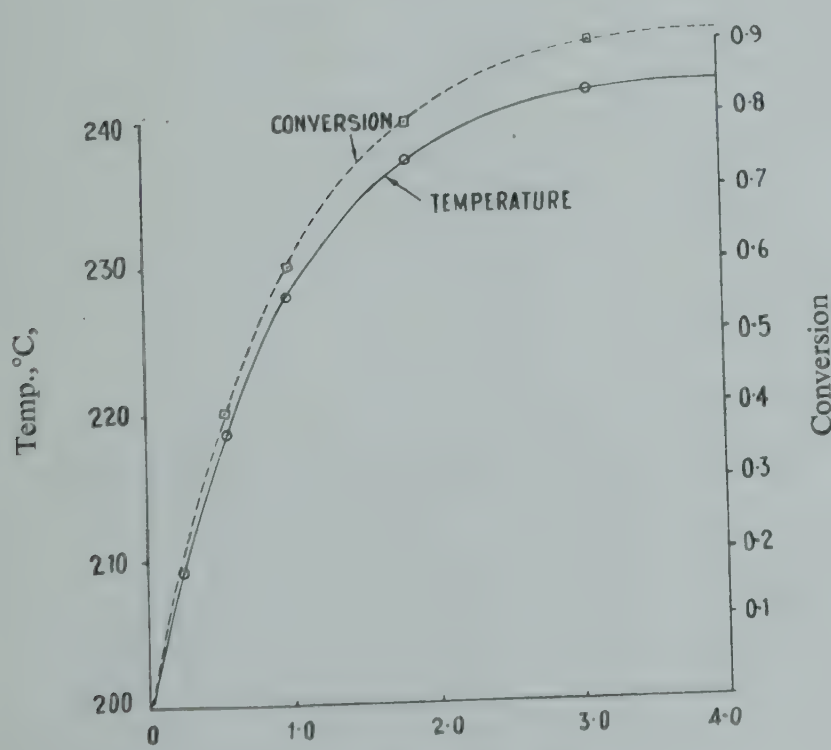
$$k_d = k \times 1.24 \tag{12}$$

The results of calculation for the L.T. catalyst obtained in an identical manner are given in Table 5 and the temperature and conversion profiles are shown in Fig. 6.



Catalyst Bed Depth, metre

Fig. 5—Variation of Temperature and Conversion with Catalyst Bed Depth for H.T. Catalyst



Catalyst Bed Depth, metre

Fig. 6—Variation of Temperature and Conversion with Catalyst Bed Depth for L.T. Catalyst

For checking the validity of the procedure illustrated above, the calculated values for H. T. catalyst were compared with the actual performance data of the reactor considered in our case study.

	Calculated	Actual
Temperature Inlet	350°C	350°C
" Outlet	375°C	377°C
% CO Leakage	2.9	3.0
Catalyst bed height	3.5 m	3.6 m

The close agreement between the calculated and actual figures indicates that the approach suggested may be considered appropriate.

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The effect of pressure and catalyst particle size on the rate of water gas shift reaction on copper-zinc catalyst has been studied. The rate of reaction under the experimental conditions studied increases with pressure, the effect of pressure being more marked on bigger size particles. This has been explained as due to the availability of larger area of internal surface of the catalyst. The Arrhenius behaviour of the reaction rate is observed in the range 150-200°C, beyond which linearity disappears. The results indicate that the activation energy of the reaction differs very slightly as the catalyst particle size is varied. An expression for the evaluation of specific rate is suggested. From a comparison of the experimental value of the effective diffusion coefficient with the calculated values, it has been shown that the nature of diffusion into the pores of the catalyst at the reaction temperature of 170°C lies in the transition region.

Low Temperature Water Gas Shift Reaction: Effect of Pressure and Particle Size on the Rate of Reaction on Copper-Zinc Catalyst

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Introduction

Extensive information on the behaviour of the water gas shift reaction over chromia-promoted iron oxide catalyst working in the range 350-500°C is available.[1-7]

The studies pertaining to the preparative and kinetic aspects of the low temperature shift catalyst operating in the range 180-250°C are recent[8-12] and not as exhaustive as the chromia-promoted iron oxide catalyst. The present catalyst is essentially a copper-zinc oxide system with various promoting components. Kasaoka *et al*[11] have compared the activities of CuO-Cr_2O_3-ZnO and Fe_2O_3-Cr_2O_3 catalysts in terms of their rates of the reaction. The rate of the reaction and its inhibition through poisoning by sulphur compounds have been studied by Morita *et al*[12]. They have given the rate as a function of the rate constant, the equilibrium constants of adsorption for carbon monoxide, hydrogen, carbon dioxide and water respectively and their partial pressures.

The present investigation is concerned with the dependence of the rate of reaction on the particle size of the catalyst under different system pressure and the evaluation of an empirical expression for the rate.

Experimental

The catalyst for the present investigation is a commercial low temperature copper-zinc conversion catalyst.

The catalyst samples for investigations were of the following sizes: (A) 6×6 mm. tablet, (B) 3×6 mm. tablet, (C) 3.35+2.41 mm., (D)—2.06+1.68 mm. and (E) −1.00 +0.776 mm. granules. The last three sizes were prepared by crushing the 6×6 mm. tablets and sieving them into respective fractions. The feed gas, obtained from the steam-reformation of naphtha, having the following composition (per cent by volume) was used: carbon dioxide 13-14, carbon monoxide 14-15, hydrogen 64-66 and methane 5-6.

The details of the arrangement for testing the catalytic activity were similar to those described earlier.[4–5] All the experiments were conducted at practically isothermal conditions, removed far away from equilibrium conversions and favouring kinetic regime. A small amount (20 cc.) of the catalyst sample, diluted 7-8 times with alumina of similar size, was taken for each set of experiment conducted under the following conditions: space velocity (hr^{-1}) 14,000-15,000, steam-to-gas ratio 0.5, temperature 160-210°C and pressure 1-12 kg/cm.^{2} The effect of increasing pressure was observed on catalyst samples A, C and D. The samples A, B and E were used to study the Arrhenius behaviour of reaction rate; further, sample E was used for evaluation of intrinsic activity. The catalyst samples were reduced at 180-190°C, with higher proportion of steam at the initial stages of the reduction; full gas load and other desired conditions were employed after complete reduction of the catalyst. The catalyst samples did not show any deterioration and retained the initial activity after the experiments.

Physico-chemical measurements were done on fresh samples. The pore size distribution was measured by the mercury penetration method. The total pore volumes were determined by mercury and helium displacement and the surface area by BET methods.

Results

The pore size distribution, surface area, etc. of the three samples are given in Table 1.

The results have been represented according to the following conversion equation, taking the rate as the the first order with respect to carbon monoxide in a flow reactor[3].

$$K_a = SV_w \log \frac{1}{1 - X/Xe} \qquad \ldots\ldots(1)$$

where K_a = Apparent activity (hr^{-1}),

$$SV_w = \frac{\text{Vol. of inlet gas + steam,}}{\text{(Catalyst volume) (hour)}}$$

X = CO converted,
Xe = CO converted at equilibrium.

In particular, the rate of mass transfer from the gas phase to the catalyst surface has a significant effect on the overall rate of the reaction conducted in laboratory type reactors. Since in kinetic studies, it is necessary to avoid this effect the magnitude of the mass transfer factor was calculated using the relation as given by Rethven[7]:

$$\eta' = 1 - \frac{Ko(d)^{1.5}}{10.9\ (Du)^{0.5}} \qquad \ldots\ldots\ldots(2)$$

where η' = mass transfer factor,
Ko = apparent rate constant based on unit catalyst pellet volume, $sec.^{-1}$
d = catalyst particle diam., cm.
D = gas phase diffusivity, $cm^2\ sec.^{-1}$
u = superficial gas velocity, $cm.\ sec.^{-1}$

The mganitude (0.992-0.998) was negligible for our experimental conditions.

TABLE 1—Pore Size Distribution Surface Area, Etc. of the Catalyst in Different Sizes

Pore Size Dist. / Radius, Å	6×6 mm. Tablet, Vol. %	−3.35+2.41 mm., Vol. %	−2.06+1.68 mm., Vol. %
4-60	0	0	0
60-100	4.9	5.9	4.8
100-175	45.0	58.2	57.8
175-300	27.5	23.7	22.1
300-400	1.9	2.0	2.9
400-500	1.3	0.6	1.7
500-75,000	9.4	9.6	10.6
Average pore size, r, Å	165.60	178.6	200.8
Total pore volume, g./c.c.	0.2294	0.2410	0.2410
Sp. surface area $m^2/g.$	27.7	26.97	26.0

The effect of pressure has been studied at four different pressures (Table 2) which are incorporated in Fig. 1. Kap/Ka_1 represents the ratio of apparent activity at a given pressure to that at atmospheric pressure.

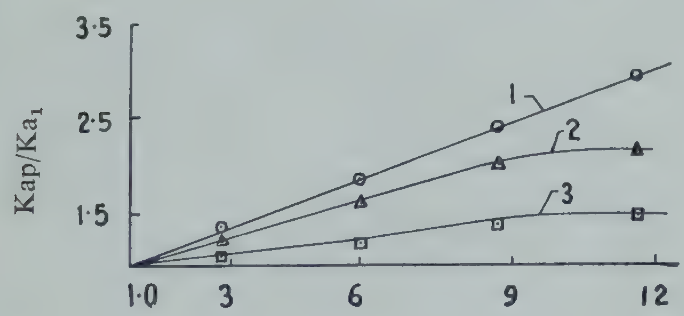
The activity of the catalyst samples A, B and E with respect to temperatures is shown in the Arrhenius plot (Fig. 3). The activation energy is calculated from the straight line portion of the curve and the pre-exponential

TABLE 2—CATALYTIC ACTIVITY VS PRESSURE

Sample	Pressure, kg/cm^2	$S.V. hr^{-1}$	Fraction of CO Converted		$Ka \times 10^{-3} hr^{-1}$	Kap/Ka_1
			Actually Converted	Converted at Equilibrium		
6×6 mm. Tablet	Atm	13,574	0.943	15.255	0.56	1.0
	3	13,514	1.421	15.255	0.78	1.39
	6	15,000	1.904	15.255	1.04	1.85
	9	15,000	2.140	15.255	1.35	2.4
	12	14,936	2.390	15.255	1.66	2.94
−3.35+2.41 mm. Granules	1	14,628	0.940	14.07	0.64	1.0
	3	14,826	1.300	14.04	0.83	1.18
	6	14,826	1.430	14.07	1.03	1.61
	9	14,826	1.842	14.07	1.29	2.01
	12	14,518	1.913	14.07	1.38	2.16
−2.06+1.68 mm. Granules	1	14,664	0.957	14.853	0.685	1.0
	3	14,798	1.042	14.772	0.71	1.04
	6	14,632	1.87	14.853	0.79	1.16
	9	14,664	1.360	14.312	0.95	1.39
	12	14,134	1.428	13.577	1.05	1.53

factor from the extrapolation of the curves. All these three experiments were done at atmospheric pressure.

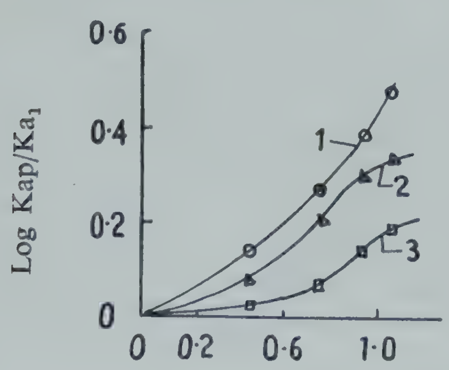
The effect of pressure on the −1.00+0.776 mm. size catalyst was observed to be negligible. This is utilized for the evaluation of the intrinsic activity, which is given by the following equation:



P, kg/cm^2

Fig. 1—Plot of Kap/Ka vs. P

1. 6×6 mm. Tablets, 2. −3.35 + 2.41 mm. Granules 3. —2.06+1.68 mm Granules



Log P

Fig. 2—Plot of Log Kap/Ka_1 vs. Log P

1. 6×6 mm. Tablets, 2. −3.35 + 2.41 mm. Granules, 3. −2.06 + 1.68 mm. Granules

$$K_v = \frac{K_a \times T}{P \times 273 \times 3600 \times \eta \times (1-E)} \quad \ldots\ldots\ldots(3)$$

where K_v = Intrinsic activity, rate constant based on unit catalyst pellet volume ($sec.^{-1}$)

K_a = Apparent activity, hr^{-1},

T = Temperature, °K,

P = Pressure, atm. (1 atm. for the case)

η = Effectiveness factor,

E = Voidage of the bed,

The effectiveness factor, η, is given by the relation

$$\eta = \frac{3}{\phi}\left[\frac{1}{\tan\phi} - \frac{1}{\phi}\right] \quad \ldots\ldots(4)$$

where

$$\phi = \text{Thiele modulus} = \frac{d}{2}\sqrt{K_v/D_e}$$

where

d = effective particle diam., cm.

D_e = effective diffusion coefficient in pores of the catalyst ($cm^2\ sec.^{-1}$)

The voidage of the catalyst bed is given[8] by the relation $E = P_B/P_p$, where P_B is the bulk density and P_p is the particle density.

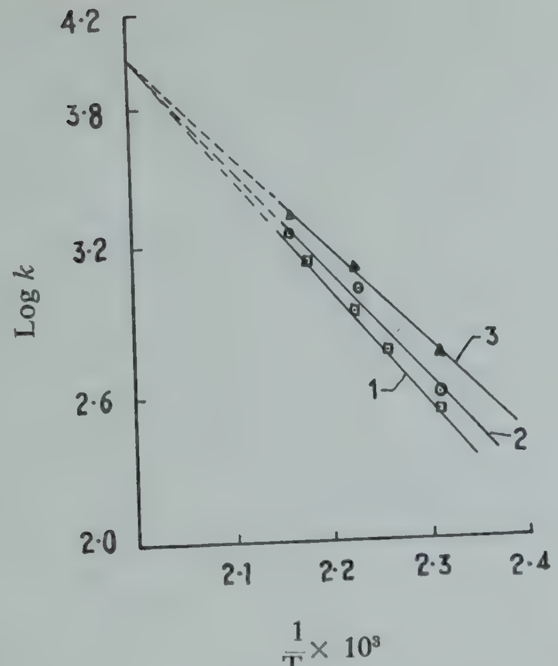


Fig. 3—Arrhenius Plot Log k vs. $\frac{1}{T}$

1. −1.00 + 0.776 mm. Granules, 2. 3×6 mm. Tablets, 3. 6×6 mm. Tablets

The intrinsic activity, K_v and effective diffusion coefficient, D_e, are obtained with the knowledge of quantities η and E. The Knudsen diffusion coefficient, D_k, is calculated from the relation $D_k = 9.7 \times 10^3 r. \sqrt{T/M}$, where r = average pore radius (Å) and M = molecular weight of the gas. The bulk diffusion coefficient, D_B, is calculated from the Gilliland formula.[13] The effective diffusion coefficient has also been calculated using the relation given by Wheeler[14]. Table 3 gives the values of ϕ and η for different samples. The values of various diffusion coefficients are shown in Table 4.

TABLE 3—THIELE MODULUS AND EFFECTIVENESS FACTOR OF THE CATALYST

Size	Thiele Modulus	Eff. Factor
6×6 mm. Tablets	0.777	0.521
−3.35+2.41 mm. granules	0.373	0.592
−2.06+1.68 mm. granules	0.42	0.634
−1.00+0.776 mm. granules	0.113	1.00

TABLE 4—VALUES OF DIFFERENT DIFFUSION COEFFICIENTS AT 170°C AND ATMOSPHERIC PRESSURE

Knudsen Diff. Coeff. D_k, $cm^2\ Sec.^{-1}$	Bulk-Diff. Coeff. D_B, $cm^2\ Sec.^{-1}$	Effective Diff. Coeff., $cm^2 Sec.^{-1}$	
		Experimental	Calculated
0.0687	0.3286	0.1296	0.0625

Discussion

From Fig. 1, it is seen that the apparent activity of the catalyst increases with increase of pressure and the bigger size particles show a more pronounced effect with change of pressure than smaller ones. It is also apparent that the availability of the internal surface of the catalyst with increase of pressure seem to approach a limiting value for the smaller sizes and incomplete in the case of 6×6 mm. tablets under the experimental range of pressure. This observation is in contrast to that of Ruthven[6], but tallies well with that of Moe[3]. Under conditions of small diffusional resistance, Ruthven[6] gives the relation $Kap/Ka_1 = P.^{0.7}$. Taking $Kap/Ka_1 = P^x$, where P = system pressure in atmosphere, the exponential factor x at different system pressures for the respective catalyst particle sizes is obtained from the plot of log (Kap/Ka_1) vs log P (Fig. 2). It is seen that the values of x differ as the particle size and the system pressure are varied; that is, for a particular pressure, the values of x are different for different sizes of the catalyst particle, and for the catalyst of a particular size, x is different with respect to pressure. It may also be observed that the exponential factor, x, increases at a faster rate for bigger size catalyst pellets and the effect is more pronounced at the higher pressure region under the experimental conditions studied. It is known that in a higly porous structure the reaction rate is controlled by the rate of mass transfer to the catalyst surface constituted by the finer pores; the increase of pressure makes the finer pores available for reaction and hence the ratio Kap/Ka_1 increases. From Fig. 2, it appears that while the exponential factor tends to approach the limiting value of zero for samples C and D, and therefore the ratio Kap/Ka_1 tends to run parallel to the P axis, the approach to the limiting value is yet to appear in the case of sample A, under the range of pressure studied. It is, therefore, likely that the exponential factor, x, would depend on the pore geometry of the catalyst particles.

The structural parameters of the catalyst samples (Table 1) were almost identical and the only difference was in the sizes of the catalyst particles. The intrinsic activity, K_v, was evaluated from the activity data on the sample −1.00+0.776 mm. granules over which the effect of pressure was found to be negligible. The effectiveness factor of this sample was taken as unity. The values for intrinsic activity are given below:

Temp.,°C	160	170
K_v, sec^{-1}	0.4929	0.8394

The Thiele modulus and the effective diffusion coefficient on this catalyst sample at the temperature of 170°

were evaluated from equation 4. The value of the effective diffusion coefficient, although close to Knudsen range, reflects that the nature of diffusion into the pores of the catalyst lies in the transition region. Ruthven[6], working with high temperature shift catalysts of bidisperse pore size distribution —where diffusion into the macropores is important diffusional resistance—found the diffusion to be molecular in nature. It is, thus, plausible that the activity of the two types of catalysts with respect to pressure would be different because of the difference in the pore structure of the catalysts.

The activation energy was calculated from the straight line portion of the curve. The pre-exponential factor is obtained from extrapolation. It is seen that the value of the activation energy varies slightly; the slight increase in value is noticed as the particle size is reduced:

Catalyst size	6×6 mm tablet	3×6 mm tablet	-1.00 $+0.776$ mm granule
Activation energy, Kcals	20.28	20.74	20.96

However, the pre-exponential factor was found to be identical in all the cases. The factor comes out as 1.072×10^4. Taking the average value of the activation energy as 20.66 Kcals, the empirical expression for the rate constant for the temperature range (150-200°C), upto which the Arrhenius law is found to be obeyed, is given by:

$$K = 1.072 \times 10^4 \text{ ex } (-20{,}660/RT)$$

The bending of the Arrhenius plot at temperatures beyond 190°C points to the transition to the diffusion regime from the kinetic regime existing in the low temperature side.

Acknowledgement

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The changes in the structural parameters of zinc oxide effected by heat treatment have been studied. Specific surface area and pore volume decrease with increasing temperature but particle size and bulk density follow the reverse order. The change in the structural parameters by heat treatment when temperature is raised from 200 to 400°C is only marginal; however, beyond 500°C there is a sharp change. The activity of the oxide does not appear to have any linear relation with structural parameter except pore size distribution. The specific pore spectrum lying between 100 and 300 Å seems to be controlling the activity of the oxide. Data on the pore size distribution of the used oxide confirm this view.

Effect of Heat Treatment on Structural Parameters and Activity of Zinc Oxide

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It is well-known that structural and textural properties play an important role in determining the activity and stability of a catalyst. While activity is one of the principal considerations for selection of a catalyst, mechanical stability and life are equally important for industrial use. A catalyst may have high initial activity but if the activity is not sustained or the catalyst gets crumbled in its use, it may have only limited application in commercial plants.

Earlier work[1] done in this laboratory indicates that activity of zinc oxide for hydrogen sulphide absorption has no direct dependence either on surface area or pore volume but pore size distribution appeared to be controlling the activity.

It is considered that for a clear understanding of the role of structural parameters, specially the pore geometry on hydrogen sulphide absorption activity and capacity of zinc oxide, a detailed study is essential.

It is known that specific surface, pore volume, pore size distribution and particle size are dependent on the method of preparation as well as chemical composition. It is possible to develop specific structural characteristics of a solid catalyst by regulating the process steps. Sintering by heating a catalyst during the process of preparation has always been used as an effective tool for attributing the desired specific structural and textural character[2]. During the process of sintering, primary particles may swell and weld at the edges changing the pore structure and mechanical strength of the finished product[3,4]. The influence of sintering on the structural parameters of zinc oxide was studied by many workers[5-9], but there is no reference in the literature on the effect of sintering on its activity.

In the present investigation, an attempt has been made to study the changes in structural parameters effected by heat treatment and to examine if a possible relation between the physical parameters and activity can be drawn. For this purpose, a particular variety of commercial catalyst was taken for investigations.

EXPERIMENTAL

A typical zinc oxide mass in globule form (3-5 mm. size) suitable for hydrogen sulphide removal was taken as the starting material. The globules were heated in parts from 200 to 900°C at an interval of 100°C for 4 hours.

Surface Area, Pore Volume and Pore Size Distribution

Measurements: Surface area was determined from nitrogen adsorption isotherm using a conventional BET apparatus. The molecular cross-sectional area of nitrogen was taken as 16.2Å^2. The evaluation of total pore volume, average pore radius (r_p) and average grain radius (r_g) was done by an earlier method.[10]

The pore size distribution was determined on the principle of mercury penetration using Aminco porosi-

TABLE 1—Effect of Heating on Structural Parameters of Zinc Oxide (Fresh)

Curing Temp., °C	Bulk Density, g./cc.	Activity (total % fouling)	S.A., m^2/g	Hg Displacement, cc./g.	He Displacement, cc./g.	T.P.V., cc./g.	Total Porosity, cc./100 cc.	Pore Size Distribution, % by volume						
								4-60 Å	60-100 Å	100-200 Å	200-300 Å	300-400 Å	400-500 Å	500-75000 Å
200	1 09	42.07	37.3	0.5232	0.1808	0.3424	65.4	4.5	13.6	68.4	9.1	1.2	0.6	2.6
300	1.10	36.83	37.2	0.5240	0.1818	0.3422	65.3	0.3	14.1	63.7	15.8	2.7	0.8	2.6
400	1.11	31.69	37.0	0.5266	0.1791	0.3475	66.7	0.0	9.4	62.4	22.7	1.4	0.7	3.4
500	1.17	17.70	29.9	0.5135	0.1821	0.3415	65.2	0.0	2.8	48.4	34.5	1.2	0.3	13.2
600	1.28	4.26	15.1	0.4787	0.1796	0.3041	63.5	0.0	1.0	9.5	58.1	22.4	4.5	4.5
700	1.43	2.81	11.8	0.4325	0.1793	0.2532	58.5	0.0	0.5	3.4	29.7	48.0	13.8	4.5
800	1.50	Nil	4.42	0.4032	0.1757	0.2306	57.1	0.0	0.1	0.6	0.9	1.4	5.9	91.1
900	1.95	Nil	1.63	0.3341	0.1741	0.1600	46.9	0.0	0.0	0.0	0.7	0.0	0.2	99.1

TABLE 2—Change in Structural Parameters After H_2S Absorption

Curing Temp., °C	S.A., $m^2/g.$	He Displacement cc./g.	Hg Displacement, cc./g.	T.P.V., cc./g.	Total Porosity, cc./100 cc.	Pore Size Distribution, % by volume						
						4-60 Å	60-100 Å	100-200 Å	200-300 Å	300-400 Å	400-500 Å	500-75000 Å
200	21.0	0.2326	0.4093	0.1767	43.2	3.0	11.0	53.8	17.1	3.3	1.9	9.9
300	23.9	0.2251	0.4900	0.2649	54.1	2.1	10.1	55.1	23.8	3.0	0.6	5.1
400	29.8	0.2041	0.4923	0.2882	58.5	6.5	7.9	57.6	19.5	2.6	0.9	4.9
500	19.1	0.2097	0.4606	0.2509	54.3	8.8	6.2	59.2	18.1	2.9	0.9	3.9
600	13.1	0.1869	0.4601	0.2732	59.3	1.8	1.0	7.0	57.0	25.5	4.4	3.3
700	11.8	0.1851	0.5169	0.2318	64.1	12.2	0.4	3.2	31.9	39.4	9.8	3.1
800	4.4	0.1792	0.3912	0.2120	54.1	0.0	0.0	0.6	0.9	3.7	11.1	83.7
900	1.64	0.1700	0.3112	0.1412	45.3	0.0	0.0	0.5	0.7	0.4	0.4	98.0

meter working upto 15,000 lbs/sq. in., pressure for the purpose of precise characterization of textural changes.

Activity Measurements: Activity measurements were made in a flow system at atmospheric pressure using an apparatus described earlier[1]. The reacting gas containing 2000-2500 ppm. of hydrogen sulphide passed in downflow direction through the catalyst bed. In each experiment, 20 c.c. of catalyst was charged and the bed was maintained isothermal at 400°C. The top and bottom temperatures of the bed did not differ by more than 5°C. A fixed space velocity of 3000 vol/vol cat/hr was maintained throughout. The experiment was continued till hydrogen sulphide could be detected in the effluent gas.

Results

The physical parameters, like specific surface area, pore volume and pore size distribution data, of the fresh oxide are given in Table 1 and the corresponding values for the used samples in Table 2. Table 1 also includes data on the activity of the catalyst. Here the maximum fouling of the oxide before hydrogen sulphide appeared in the effluent gas is taken as an index of activity. As the other kinetic factors, such as space velocity and partial pressure of hydrogen sulphide in the feed, were kept constant in all the experiments, the maximum fouling as an index of activity may be considered reasonable at least for comparative purpose.

Pore volume computed from mercury and helium displacement volumes (Tables 1 & 2) was estimated by a conventional helium densitometer. Pore size distribution values have been presented in seven steps starting from 60 to 75,000Å.

Average pore radius (r_p) and particle radius (r_g) and their ratio (r_p/r_g) are given in Table 3. The dependence of activity on particle and pore radius is shown in Fig. 2.

The dependence of hydrogen sulphide absorption activity on specific surface and the corresponding curing temperature are plotted in Fig. 1. A comparison of the specific activities can be made by dividing the activity with specific surface area.

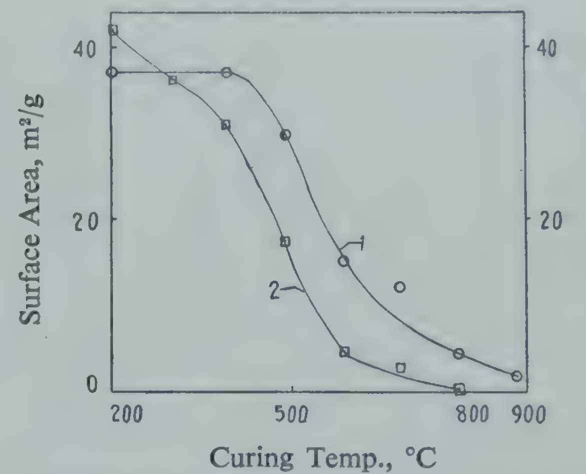


Fig. 1—Dependence of Surface Area and Activity of Curing Temperature

1. Surface Area, 2. ZnO Sulphided, %

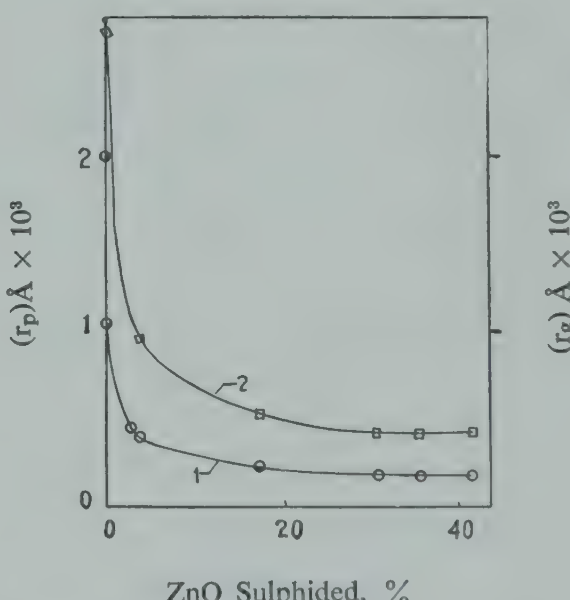


Fig. 2—Dependence of Activity on Pore and Particle Radii

1. Average Pore Radius, r_p
2. Average Particle Radius, r_g

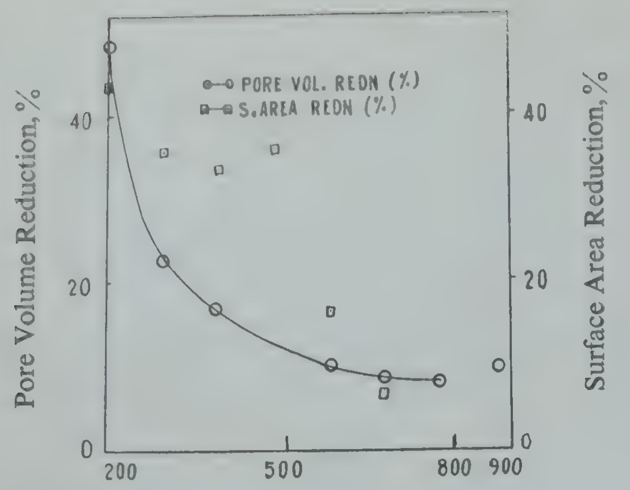
TABLE 3—Effect of Heating on Pore and Particle Size

Curing Temp., °C	Average Pore Radius (r_p), Å	Average Particle Radius (r_g), Å	r_p/r_g
200	183.7	420.8	0.435
300	183.9	422.6	0.435
400	187.8	426.9	0.439
500	228.4	515.2	0.443
600	402.8	951.0	0.423
700	429.1	1099.5	0.3904
800	1043.4	2735.9	0.381
900	1963.1	6149.0	0.319

There has been a considerable reduction in pore volume and specific surface area of the oxide mass after use. The changes in these two physical parameters computed as percentage reduction are presented in Fig. 3.

Discussion

Zinc oxide, which is commonly known as a desulphurization catalyst, reacts with hydrogen sulphide and fixes it as zinc sulphide. Its activity will evidently depend on the available oxide molecule on the surface of the solid contact mass and the ease of transport of the gaseous reactant on the solid reactant surface. As the starting



Curing Temp., °C

Fig. 3—Reduction in Pore Volume and Surface Area after Use

materials of the zinc oxide catalyst studied in this investigations comes from the same parent body, their activity is likely to depend only on their structural parameters and pore geometry.

It has been observed that there is a wide variation in the absorption capacity of the samples studied and this has been clearly reflected in their structural and physical parameters. It is further observed that heat treatment of the oxide beyond a limit leads to rapid sintering of the particles resulting in considerable decline in activity. The study also indicates the maximum reaction temperature to derive a sustained hydrogen sulphide retention activity of zinc oxide.

Bulk Density: Zinc oxide melts above 1800°C but it may be seen that the shrinkage of the oxide mass starts right from 200°C and the bulk density increases progressively upto 900°C. At 200°C it has a bulk density of 1.09 g./cc, which increases to 1.95 g./cc. at 900°C. The true density of zinc oxide in the crystalline form is 5.606 g./cc. It appears that the densification of the oxide has accelerated above 500°C and the volume shrinkage is maximum between 800-900°C.

Specific Surface, Pore Volume, Pore Size Distribution and Activity: On the basis of specific surface area and pore volume, the oxides investigated may be classified into three distinct groups. Upto 400°C there is practically no change in these parameters (Table 1). Specific surface decreases by about 60 per cent in the second group as the curing temperature increases from 400 to 600°C. In the next group when the temperature is raised to 900°C, the surface area dropped by about 90 per cent from 15.1 m^2/g (600°C) to 1.63 m^2/g (900°C). Similarly, the pore volume dropped by about 12 per cent in the first step and 50 per cent in the second, when the curing temperature is changed from 600 to 900°C. It may be seen that reduction in surface area is comparatively larger than that in case of pore volume reduction. This may happen if the disappearance of the smaller pores is accompanied by the simultaneous creation of new pores. In such a case, though there may be a considerable reduction of surface, pore volume reduction may be comparatively small (Table 1). The sample cured at 200°C has 96 per cent of the pore volume in the micropore region. These micropores disappeared completely when the mass was exposed to 900°C. Thus, pore volume 0.1600 cc/g. of the mass cured at 900°C must be in the macropore region and these pores obviously appear at the expense of the finer pores. The contribution to surface by these larger pores obviously will be only marginal.

The surface area (Table 2) of the sulphided mass is considerably reduced after use, but it does not follow a regular pattern as pore volume changes (Fig. 3). This may happen when activity does not bear any linear relation with the specific surface. This may also happen if the absorption of hydrogen sulphide is not uniformly spread throughout the mass. The reduction in surface area is appreciable for the oxides having a large initial surface and high activity. For oxides cured at high temperature, surface area remains unchanged even after use; of course, those produced at 800 and 900°C are practically inactive and did not absorb any measurable quantity of hydrogen sulphide.

The percentage reduction of pore volume follows a regular pattern. The reduction has been maximum (Fig. 3) for the oxides cured at lower temperatures. In the present investigation, absorption of hydrogen sulphide has been effected at 400°C, and the oxides cured upto 400°C have practically identical pore volume. The reduction in pore volume in the case of the used oxides, therefore, must be due to the sulphidation in the pores. As such, reduction of surface is likely to be proportionately larger in the samples having a higher proportion of micropores contributing to higher activity. But there seems to be some thermal influence too because even in case of the comparatively inactive oxides which did not absorb any hydrogen sulphide there is about 10 per cent reduction in pore volume.

Pore Spectrum: The pore spectrum of the fresh and used samples have some notable features (Tables 1 & 2). Only the sample 1, cured at 200°C, has 4.5 per cent pore volume upto 60Å; oxides cured at lower temperature in general have proportionately larger pore volume with finer pores. With increasing temperature of curing, this range of pores having radii 200Å and below progressively decreased. The oxide, heat-treated at 200°C, has 87.5 per cent pore volume with pores having maximum radius

of 200Å only. The pores in this range have completely disappeared at 800°C. However, in case of oxide cured at 900°C the total reduction of pore volume is only slightly over 50 per cent. Therefore, the disappearance of the pores has been partly compensated by simultaneous creation of wider pores. This will be evident if we move downwards from top to bottom (in Table 1). The newly created pores have made appearance between 400 and 75000Å range. The data on pore size distribution may be used as a valuable guide for selecting heat treatment temperature during production of zinc oxide.

The pore spectrum of the used oxides throws light on the probable mechanism of the filling up of the pores. Some micropores have been seen in the sulphided mass which did not exist in the fresh oxide and at the same time there has been reduction of the pore volume in the range 100-300Å. This is quite significant and gives an indication about the specific pore range effective in sulphur fixation. If the sulphur is deposited in the pores falling between 100 and 300Å region mainly, it is possible that the pores will be further subdivided to lower size and the spectrum will be shifted to the left-hand region. It was observed in an earlier investigation[1] that pore volume upto 500Å is probably the most effective region for absorption of hydrogen sulphide. The present investigation gives further support to the earlier observation.

There have appeared new pores in the range of 200 to 300Å, which is a deviation from the general trend. This has probably occurred by the widening of the pores due to thermal effect only; because there is no simultaneous reduction of the pore volumes in the higher range.

Relative Change of r_p *and* r_g: In case of fresh oxides (Table 3), particle size and average pore radius have increased with increasing temperature of heating. Upto 400°C the changes in these parameters are only marginal. From 500°C and upwards the change is quite sharp but the relative change is not the same throughout. When the temperature is increased to 600°C and above, the particle size increases at a faster rate (Table 3) than the pore size. The average pore radius has increased ten-fold on varying the temperature from 200 to 900°C. For the same temperature rise, particle radii have increased fifteen-fold.

Activity and Structural Parameters: The relations of surface area and activity with curing temperature and activity with pore and particle size are shown in Figs. 1 & 2 respectively. The oxide mass heated at 200°C is most active with about 42.0 per cent absorption capacity. All the oxides heated upto 400°C have almost identical specific surface but the activity is considerably lower in case of the sample heated at 400°C when compared with that heated at lower temperatures. Obviously, it indicates that activity is not a direct function of surface area but any change in it with simultaneous shift of the distribution of pores with curing temperature indicates dependence of activity on pore size distribution. A shift of pores in the high diameter region causes lowering of activity. In the case of both surface area and activity, there is a sharp change beyond 400°C which is most prominent between 400-600°C. Though there is a parallelism in the pattern of the two curves, the activity drops at a faster rate than the surface area for the same temperature rise. At a still higher temperature of heat treatment, the surface area decreases further but the residual surface area has no contribution on activity. Therefore, it appears that an oxide with good activity may be obtained by heating it between 200 and 400°C. A similar observation was made in the earlier investigation[11] where heating the oxide at lower temperature gave the mass a superior activity.

There is no linear relation of activity with average pore and particle sizes. These two parameters may only be utilized to indicate the activity of the mass qualitatively. It is clear that an active zinc oxide must have pore and particle size in the lower range. An oxide with good activity should have pores of size preferably near 200Å and particle size 500Å. Such structural geometry may be generated and stabilized in the lower temperature region below 400°C. Increase in temperature beyond this limit progressively eliminates the pores responsible for higher activity of zinc oxide mass.

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A method for the determination of surface area of copper in the reduced low temperature shift catalyst (CuO-ZnO type) by carbon monoxide oxidation has been suggested. The combined surface area of zinc oxide—determined by hydrogen adsorption—and copper in the reduced catalyst has been found to be in good agreement with the total BET surface area. The dependence of catalytic activity on the surface area of copper has also been discussed.

Determination of Surface Area of Copper in a Low Temperature Shift Catalyst

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Introduction

The measurement of the degree of dispersion of the active component of a catalyst helps to obtain valuable information about the optimum conditions for catalyst preparation, relationship between catalyst activity and active surface area and the effect of aging on catalyst. In the low temperature shift catalyst where copper is the active component, 'spacer' materials, like zinc oxide, aluminium oxide, chromium oxide, etc., are used to minimize the effect of sintering and retain the finely dispersed state of reduced copper. Hence, the usual methods for determining surface area of dispersed metals by hydrogen or carbon monoxide chemisorption cannot be applied in cases where zinc oxide is present, as it will adsorb both the gases.

Uchida[1] has calculated the surface area of copper S_{Cu} using the formula,

$$S_{Cu} = S - S_1 \times W$$

where S = total surface area/g. of the reduced catalyst,

S_1 = surface area/g. of zinc oxide alone, and

$$W = \frac{\text{Weight of ZnO}}{\text{Weight of (ZnO+Cu)}}$$

In this calculation it is assumed that zinc oxide and copper exist as two separate phases in the catalyst, the catalyst surface area is the sum of the surface areas of zinc oxide and copper particles and that the zinc oxide powder does not undergo any change in surface area during preparation or reduction. However, the applicability of this equation and the validity of the assumptions involved can be verified only if the method of preparation of the catalyst is known.

Osinga *et al*[2] have studied the decomposition of nitrous oxide on copper supported on alumina and have shown that the amount decomposed is 0.176 cc. N_2O/m^2 of copper

$$N_2O \rightarrow N_2\ \text{gas} + O_{ads}.$$

Thus, from the amount of nitrogen formed which is equal to the amount of nitrous oxide decomposed, one can calculate the surface area of copper.

Direct chemisorption of oxygen cannot be a suitable method for the determination of the surface area of reduced copper, though in this case there will be negligible interference due to adsorption on zinc oxide. Rhodin[3] has shown that copper suitably activated by treatment with hydrogen is readily oxidized at all temperatures and the thickness of the oxidized layer increases with increasing temperature. By careful oxidation at low temperature, the oxidized state is limited to the cuprous oxide stage and at −195°C the oxide layer thickness does not exceed 4Å. In this case it is expected that the surface area of copper will remain practically same before and after oxidation. The validity of such an assumption is supported by results of surface area measurements. Jennings and Stone[4] have shown that this cuprous oxide layer on copper—henceforth designated as Cu_2O/Cu system—can readily chemisorb oxygen at temperatures as low as −70°C but only the adsorptions at room temperature and

above can give rise to a monolayer coverage. Kholyavenko *et al*[5] have measured the oxygen chemisorbed at 20°C by cuprous oxide supported on silicon carbide and alumina and found it to be constant, viz. 0.114 cc(NTP)/m^2 Cu_2O, irrespective of the degree of dispersion of cuprous oxide. According to Jennings and Stone[4], as the room temperature chemisorption approaches a monolayer in Cu_2O/Cu systems, cuprous ions move into the interstices of the adsorbed layer binding the adsorbed oxygen as oxide ions and thus produce new sites for further adsorption. Consequently, cation vacancies will be created in the oxide layer which will be filled up by cuprous ions moving in from the underlying metal. Thus, in a Cu_2O/Cu system the total uptake of oxygen at room temperature will greatly exceed the monolayer value unless the pressure is as low as 0.06 mm. Hg. Hence in this case, measurement of copper surface area by direct measurement of oxygen chemisorption will introduce gross errors.

The difficulty can be overcome if a distinction is made between the adsorbed and absorbed oxygen. Garner *et al*[6] have shown that adsorption of oxygen occurs through dissociation at an anionic vacancy in the surface which permits one oxygen atom to enter the lattice, the other being free to move over the surface. This mobile oxygen atom is highly reactive and readily reacts at room temperature with carbon monoxide to form the carbonate ion complex. In presence of excess of carbon monoxide, the complex breaks up to give carbon dioxide which evaporates. The various steps in the process are shown below.

$$O_{2gas} \rightleftharpoons O_{2ads} \rightarrow O_L + O^{\mp},$$

where O_L is the oxygen atom bound to the lattice, $O^{\mp}$, representing the free atom. $O^{\mp}$ can form a semi-conducting ion pair with Cu^+ ion.

$$O^{\mp} + Cu^+ \rightarrow Cu^{2+} + O^-$$

The O^- then reacts with CO

$$2O^- + CO_{gas} \rightarrow CO^{2-}{}_{3ads}$$
$$CO^{2-}{}_{3ads} + CO_{gas} \rightarrow 2CO_2 + 2e$$

Thus, only 50 per cent of the adsorbed oxygen atoms react with carbon monoxide at room temperature. In other words, from the amount of carbon dioxide formed it is possible to calculate the surface area of the cuprous oxide layer, as 5.2×10^{18} sites/m^2 are occupied by adsorbed oxygen atoms on cuprous oxide at room temperature.

In the present investigation, catalytic room temperature oxidation of carbon monoxide by oxygen has been utilized to estimate the amount of oxygen adsorbed on cuprous oxide. This reaction is characteristic of cuprous oxide and there will be no interference by the other oxides present in the L.T. catalyst as they catalyse the reaction only at higher temperatures.

It is quite reasonable to think that some lattice oxide ions may also react with carbon monoxide. From isotope exchange studies, Winter[7] has shown that lattice oxygen can be extracted from cuprous oxide at room temperature and below, but this is limited only to a very small number of sites.

Experimental

Materials: The catalysts used are all of commercial variety. They contain about 33 per cent copper oxide, 66 per cent zinc oxide and 1 per cent iron oxide. The original cylindrical tablets of 6 mm$\times$6 mm size were ground in an agate mortar and sieved to $-16+20$ mesh size (BSS). Hydrogen obtained from M/s Indian Oxygen Ltd. was purified by passing through a DeOxo tube and then dried by passing through towers containing silica gel and magnesium perchlorate. Carbon monoxide was prepared by dehydration of formic acid by concentrated sulphuric acid and purified by bubbling through caustic potash solution and finally dried by passing through a liquid nitrogen trap. Nitrogen obtained from M/s Indian Oxygen Ltd. was passed through reduced copper at 500°C and dried by liquid nitrogen trap. Helium obtained from M/s Matheson & Co. was used as such without further purification. All the gases used were analysed by a Griffin D-6 gas chromatograph. The nitrogen used contained about 0.05 per cent oxygen. The oxygen content of other gases was found to be negligible. All the adsorption measurements were carried out in a conventional all-glass volumetric apparatus.

Reduction of Catalyst: About 15 cc of the catalyst was taken in a reactor tube (Fig. 1). The temperature was measured by a chromel-alumel thermocouple connected to a Mahindra temperature indicator. The catalyst was reduced carefully at 200°C in a stream of pure and dry hydrogen. To stabilize the surface, the hydrogen flow (5 1/hr) was continued for 24 hours at 200°C. Then the end of the exit tube was plugged by means of a cap with a B-7 socket, hydrogen flow was cut off, the sample was evacuated and the exit tube was sealed off at the constriction B.

Cleaning of the Surface: The reduced sample was evacuated at 200°C to a pressure of 10^{-3} mm. of Hg for $\frac{1}{2}$hr. Hydrogen was introduced at a pressure of about 150 mm of Hg and 200°C and was pumped out after 3 hours. After evacuation as before, the sample was left in contact with hydrogen for 12 hours. Finally, the evacuation

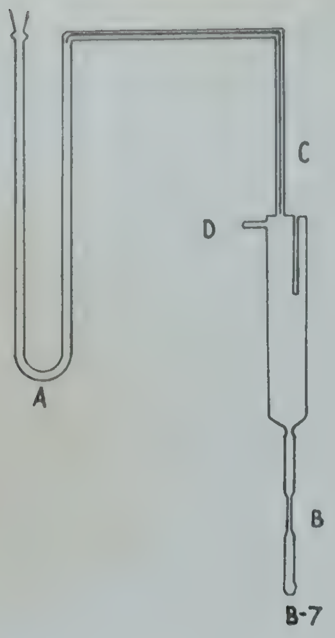

Fig. 1—Reactor Tube

was carried out for 6-7 hours to a pressure of about 10^{-5} mm. Hg. A steady pressure below 10^{-2} mm. Hg, 15 min. after the pumps were cut off, was taken to be a standard test for clean surface for all the samples.

Hydrogen Adsorption: The 'cleaned' sample was cooled in liquid nitrogen and the adsorption isotherm of hydrogen was determined (Fig. 2).

BET Surface Area: After pumping out the adsorbed hydrogen the total surface area was determined by nitrogen absorption at —196°C, taking the area of cross section of nitrogen molecule to be 16.2 Å^2.

In order to check the 'cleanliness' of the surface of the reduced catalyst after hydrogen and nitrogen adsorption measurements, the sample was left in contact with carbon monoxide at room temperature for 24 hours. No carbon dioxide could be detected which showed the copper surface adequately 'clean'.

Oxidation: The sample after surface area measurement was evacuated at room temperature for 2 hours and then cooled in liquid nitrogen. Then the sample was left in contact with oxygen at 4 mm of Hg. for 2 hours. The BET surface area was redetermined after evacuation of oxidized sample for 2 hours.

Oxygen Chemisorption: After evacuation for 1 hour at room temperature, the oxidized sample was brought in contact with oxygen at 4 mm. Hg and then after 5 min. the gas was pumped off.

Carbon Monoxide Oxidation: The trap A was then cooled in liquid nitrogen and carbon monoxide was introduced into the sample chamber at room temperature at 200 mm of Hg. After 24 hours unreacted carbon monoxide was pumped off, the reactor tube was sealed off at C (Fig. 1), the liquid nitrogen Dewar was removed, the frozen carbon dioxide was allowed to evaporate and its volume at NTP was determined.

After the completion of the experiment, the reactor tube sealed out at C was weighed. The weight of the reduced catalyst was found by the difference after removing the sample by breaking the sealed side tube at D.

Activity Measurements: The activity measurements were carried out at 200°C in an apparatus similar to the one described previously[8]. About 1 cc. of the catalyst of —16, +20 mesh size was used and diluted with 1 cc. of Pyrex glass chips of same mesh size. The catalyst was reduced

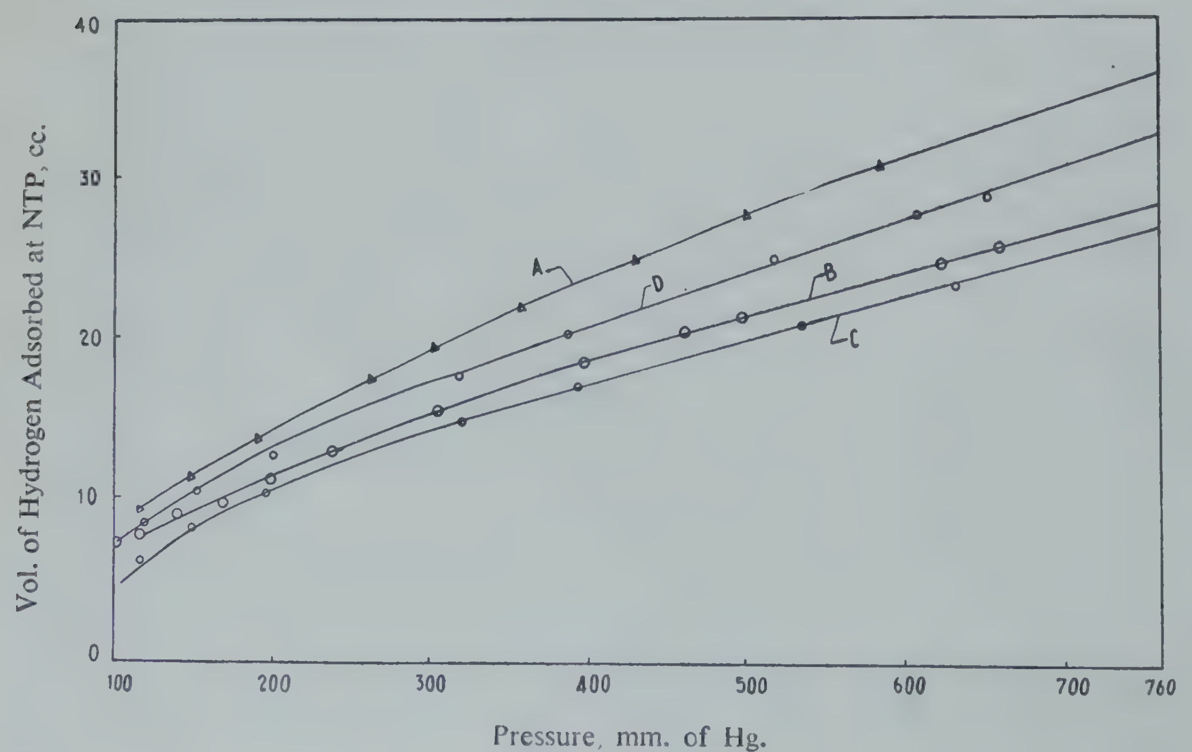

Fig. 2—Hydrogen Isotherm on Reduced LT Catalysts at —196°C

with dry hydrogen at 200°C for 24 hours. The following gas composition was used in all the experiments: carbon monoxide 5 per cent (approx), nitrogen rest and steam/gas ratio (v/v) = 1.3.

The dry gas flow rate was kept at 5 l./hr. The exit gas was analysed for carbon dioxide, by passing a known volume of the gas through specially designed absorber bottles, described by Temkin[9], containing a standard caustic soda solution. The amount of sodium carbonate formed was estimated by titration. The rate constant k_1 was calculated by using the first order rate equation.

$$k_1 = -V(R+1)\ln\left(1-\frac{\eta}{\eta_{eq}}\right)$$

When V = dry gas flow rate, cc./hr/g. of reduced catalyst,
R = steam/gas ratio, v/v
η = degree of conversion, and
η_{eq} = degree of conversion at equilibrium.

Results and Discussion

The experimental results are given in Table 1. The total volume of oxygen adsorbed (V_{O_2}) will be equal to the volume of carbon dioxide (V_{CO_2}) formed, as only 50 per cent of adsorbed oxygen participates in the reaction. The surface area of copper (S_{Cu}) which will be the same as the surface area of the overlying cuprous oxide layer (S_{Cu_2O}) can then be calculated from the data of Kholyavenko[5]. Alternatively, assuming that the oxygen chemisorption on cuprous oxide is dissociate and that there are 5.2×10^{18} sites/m² of cuprous oxide surface it is possible to calculate S_{Cu_2O}.

$$\text{Hence, } S_{Cu} = S_{Cu_2O} = \frac{2V_{O_2}\times6.02\times10^{23}}{5.2\times10^{18}}\cdot \text{m}^2 \qquad (1)$$

The values obtained by both the methods are in good agreement as can be seen in columns 3 and 4 (Table 1).

BET surface area values before and after oxidation indicate that there is no change in the area of the surface during oxidation.

In order to check the validity of the results obtained, the surface area of zinc oxide (S_{ZnO}) was measured by hydrogen adsorption. Taylor and Liang[10] have shown that zinc oxide activated by reduction with hydrogen at 400°C followed by evacuation adsorbs considerable amount of hydrogen at −196°C and the volume adsorbed at 760 mm. pressure is 80 per cent of the monolayer volume of nitrogen. From the hydrogen adsorption isotherms obtained in the present investigation (Fig. 2), the volume adsorbed at 760 mm. (H_2) was determined, Then, neglecting the volume of hydrogen physisorbed on copper and assuming the validity of Taylor and Liangs findings for zinc oxide treated with hydrogen at 200°C.,

$$S_{ZnO} = \frac{V_{H_2}\times100}{80}\times\frac{N\sigma\times10^{-23}}{22.4}\text{m}^2,$$

where σ = area of cross-section of nitrogen molecule, Å²
and N = Avogadro number.

The cumulative surface area of the catalyst $S_{Cu}+S_{ZnO}$, is in good agreement with BET surface area (S_{BET}) as can be seen from the results (columns 7 and 8, Table 1).

The activities of the different catalysts at 200°C in terms of rate constant k_1 are given in column 9. It can be seen that with increase in copper surface area the activity increases. All the 4 samples tested contain the same (33 per cent) amount of copper. But the variation in the method of preparation results in different surface copper. Hence, attempts should be made to get maximum copper distribution on the surface during the preparation. A catalyst having low percentage of copper may give better activity due to a more favourable distribution than one

TABLE 1—EXPERIMENTAL RESULTS

1	2	3	4	5	6	7	8	9
Sample	V_{O_2} at NTP, cc.	Surface Area (S_{Cu}) of Reduced Catalyst, m²/g a	b	V_{H_2} at NTP, cc.	Surface Area (S_{ZnO}) Reduced Catalyst m²/g.	$S_{Cu}+S_{ZnO}$	S_{BET} of Reduced Catalyst, m²/g.	k_1 cc./hr/g. of reduced cat.
A	1.375	12.06	14.35	2.23	12.21	26.56	28.59	3.7×10^4
B	0.79	6.93	8.17	1.52	8.33	16.50	19.3	3.3×10^4
C	0.715	6.27	7.39	0.96	5.26	12.65	11.3	2.9×10^4
D	0.613	5.38	6.34	1.20	6.57	12.91	15.18	1.8×10^4

a = calculated from Kholyavenko's data.
b = calculated from the data of Jennings and Stone.

containing higher percentage of copper. A detailed study on surface copper *vis-a-vis* catalyst preparation is in progress.

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Sintering study of alumina pellets with or without nickel oxide (NiO) has been made with particular reference to the latter's role upto 10 per cent. It has been observed that the alumina pellets show a drastic shrinkage, densification and improvement of strength in the range 1200-1500°C, whereas those containing nickel oxide show a similar effect at 1150-1400°C. Nickel oxide in small proportion enhances considerably densification of the pellets but with higher propertions the effect is very much less although the bulk density is higher than that of alumina. The strength at the high sintering temperature is found to decrease with increasing concentration of nickel oxide whereas at lower temperature the reverse is the case. It also changes the specific heat of the alumina pellets. In the case of alumina specific heat increases with sintering temperature whereas that containing nickel oxide shows a reverse trend. A possible mechanism of the role of nickel oxide in modifying the bulk structure as affected by sintering process has been discussed.

Role of Nickel Oxide on the Sintering Behaviour of Nickel Oxide-Alumina Catalysts

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Introduction

For hydrocarbon reformation with steam and oxygen, nickel oxide supported over alumina is used as catalyst. The alumina-supported catalyst is generally shaped in the form of small pellets and packed in the catalyst converter. The autothermal reformation reaction occurs usually in the range 900 to 1100°C and sometimes it may even shoot above 1300°C. In this range, the bulk properties of the catalyst pellets are likely to change as a result of sintering. Therefore, from the point of view of both assessment of suitability for commercial use and development of heat resistant catalysts, it is essential to study the sintering characteristics of alumina-carrier and extent to which these sintering characteristics are modified due to the presence of the active component, viz. nickel oxide.

The shrinkage, densification, strength, specific heat and other bulk properties on sintering depend very much on the method of preparation and the nature of the additives used. Pure alumina bodies, when prepared by dry pressing and extruding process, show the maximum bulk changes in the range 1400-1700°C[1]. Nickel oxide in small proportion (0.25 per cent by wt.) assists densification of alumina on sintering. It is believed that nickel oxidewhen added in traces acts as an inhibitor of grain growth in the alumina and is located preferentially at grain boundaries causing densification[2,3]. It is further believed that the desired inhibition of the crystal growth on firing can be attained by the addition of an oxide which forms an eutectic with the oxide under consideration and by firing the mixture below the eutectic point[1]. In the nickel oxide-alumina system, there are eutectics on both high and low sides of nickel oxide; on the lower side, the eutectic temperature is 1875°C and the eutectic compound contains 10 per cent nickel oxide.

Nickel oxide forms a spinel with alumina, which also assists the densification of the latter during the sintering process[2]. The spinalization temperature is very much dependent on the method of preparation. Spinel formation from hydroxides of aluminium and nickel, precipitated simultaneously, may occur at as low as 700°C[4]. During regeneration of nickel-alumina catalysts (oxidative phase), a partial spinel formation takes place at a still lower temperature,[5] viz. 500°C. Cobalt oxide (CoO) also forms a spinel with alumina. When cobalt oxide and γ-alumina are used, spinel formation takes place to a maximum extent at 1000°C where γ-alumina changes to α-form. With α-alumina spinel formation is slow and takes place mainly beyond 1000°C[1]. With nickel oxide there is no such data but it is expected that nickel oxide would behave similarly. However, the dependence on nickel oxide concentration of the shrinkage, densification and changesof other bulk properties of alumina bodies is not clearly understood uptil now.

Considering this, an attempt has been made in the present investigation to study the sintering behaviour of nickel oxide-alumina pellets with respect to a variation of nickel oxide concentration in the range particularly upto the first eutectic composition.

Experimental

Preparation: Samples of alumina pellets having 0, 2.5, and 10 per cent nickel oxide were prepared by using a commercial variety of alumina which contains only about 0.3 per cent sodium oxide (Na_2O) as an impurity along with traces of potassium oxide. The finely powdered calcined alumina consisting mainly of α-alumina (with minor amounts of γ-alumina), was made into a paste with nickel nitrate solution of proper concentration and the paste of a suitable consistency was extruded in an extrusion mill. The extruded rods of 10 mm. diam. were sized to 20 mm. long pellets and dried at 110°C.

Nickel oxide, formed on decomposition of its nitrate, shows a sharp shrinkage at about 800°C due to intermolecular change in its lattice structure[6]. So, to ensure complete structural shrinkage of nickel oxide all the samples were heat-treated initially at 850°C for 8 hours in an oxidizing condition. However, in the case of the pure alumina sample the same method of preparation was followed excepting that the alumina powder was made into paste with water instead of nickel nitrate solution.

Heat Treatment of the Samples: Each sample, prepared as above, was heat-treated at 1000, 1200, 1300 and 1500°C for 3 hours in an oxidizing atmosphere in an electrically-heated muffle furnace. Both heating and cooling were done inside the same furnace and the time required for heating up to the desired temperature and cooling down to room temperature was 8 to 10 hours. It was observed that the shape of the pellets was not deformed even after heat treatment upto 1500°C.

Measurement of Physical Parameters: An average of six measurements for determination of each of the following physical parameters was taken.

(1) **Volume Shrinkage**—The dimensions of each sample before and after heat treatment were determined accurately by a slide calliper. From the linear dimensions the apparent volume was calculated and volume shrinkage determined.

(2) **Bulk Density**—The weight of each sample was taken before and after heat treatment in an analytical balance. From the calculated volume, and measured weight, the bulk density of each sample was determined.

(3) **Crushing Strength**—The strength of each sample before and after heat treatment was determined in a hydraulically-operated universal type press. The crushing strength was calculated from the total crushing load and the area of cross-section of pellets.

(4) **Weight-loss**—Weight-loss was calculated from the weights of the samples before and after heat treatment.

(5) **Specific Heat**—specific heat of each sample before and after heat treatment at different temperatures, was determined at 80°C (353°K) in a differential scanning calorimeter*. The instrument was standardized with a standard sapphire sample whose specific heat at 350°K is

* Perkin-Elmer Type DSC.1B

TABLE 1—EFFECT OF NiO ON THE SINTERING CHARACTERISTICS OF ALUMINA PELLETS

Physical Properties	Extruded Alumina Pellets with									
	0% NiO, °C					2.5% NiO, °C				
	850	1000	1200	1300	1500	850	1000	1200	1300	1500
	1	2	3	4	5	6	7	8	9	10
Volume Shrinkage, %	Nil	0.79	1.42	12.32	26.63	Nil	1.07	4.06	28.67	44.51
Bulk Density, g./cc.	2.00	2.01	2.02	2.23	2.65	1.90	1.91	1.97	2.61	3.35
Crushing Strength, Kg./Cm².	140	214	255	255	1530	145	220	376	492	1050
Weight-loss, %	Nil	0.52	0.61	2.33	2.66	Nil	0.57	0.74	1.86	2.27
Specific heat, cal./g./°K (at 353°K)	0.2240	0.2245	0.2250	0.2252	0.2260	0.2308	0.2304	0.2248	0.2248	0.2200

TABLE 1—(*Contd.*)

Physical Properties	Extruded Alumina Pellets with									
	5% NiO, °C					10% NiO, °C				
	850	1000	1200	1300	1500	850	1000	1200	1300	1500
	11	12	13	14	15	16	17	18	19	20
Volume Shrinkage, %	Nil	4.04	13.02	26.66	40.47	Nil	2.62	8.54	18.38	37.53
Bulk Density, g./cc.	1.90	1.97	2.17	2.54	3.10	1.90	1.94	2.06	2.27	2.95
Crushing Strength, Kg./Cm².	192	255	465	600	884	148	150	220	410	530
Weight-loss, %	Nil	0.57	0.66	1.88	2.85	Nil	0.60	0.80	2.40	3.10
Specific heat, cal./g./°K (at 353°K)	0.2255	0.2244	0.2226	0.2221	0.2188	0.2134	0.2093	0.2075	0.2070	0.2012

0.2095 cal/g./°K. The value is accurate upto ± 0.0002. cal.

Results and Discussion

All the physical parameter data are tabulated in Table 1.

The variations of volume shrinkage, bulk density, crushing strength, weight-loss and specific heat with curing temperatures are shown in Figs. 1, 2, 3, 4 and 5 respectively.

It is evident from the results (Table 1) that in the case of the alumina sample without nickel oxide there is no shrinkage upto 1200°C. A drastic shrinkage occurs in the range 1200-1500°C. It may be mentioned here that this temperature range of drastic shrinkage is lower than that observed in the case of dry-pressed bodies. The lowering of shrinkage temperature may be due to the method of preparation and presence of an alkali in the the commercial sample of alumina. Alkali, even in small proportion, is known to change the properties of the sintered bodies as it forms compounds with alumina.[1] Alumina pellets containing nickel oxide also show similar shrinkage behaviour as pure alumina but in the former case the shrinkage temperature is slightly lower and occurs in the range 1150-1400°C (Fig. 1). The weight-loss of all the samples is observed to be maximum in the same temperature range where shrinkage is maximum as is apparent from Figs. 1 and 4. However, the maximum weight-loss observed on heating upto 1500° C is only 3.1 per cent which is very low and is not likely to play any significant role in the process of shrinkage.

Densification behaviour of these samples as observed in Fig. 2 is also in conformity with what is observed in the shrinkage sequence. It is interesting to mention here that there is an improvement of bulk density due to the incorporation of nickel oxide but the densification is maximum with 2.5 per cent nickel oxide. This densification lowers down with increasing proportion of nickel oxide. Thus, of the three nickel-bearing samples the one with 10 per cent nickel oxide shows minimum densifica-

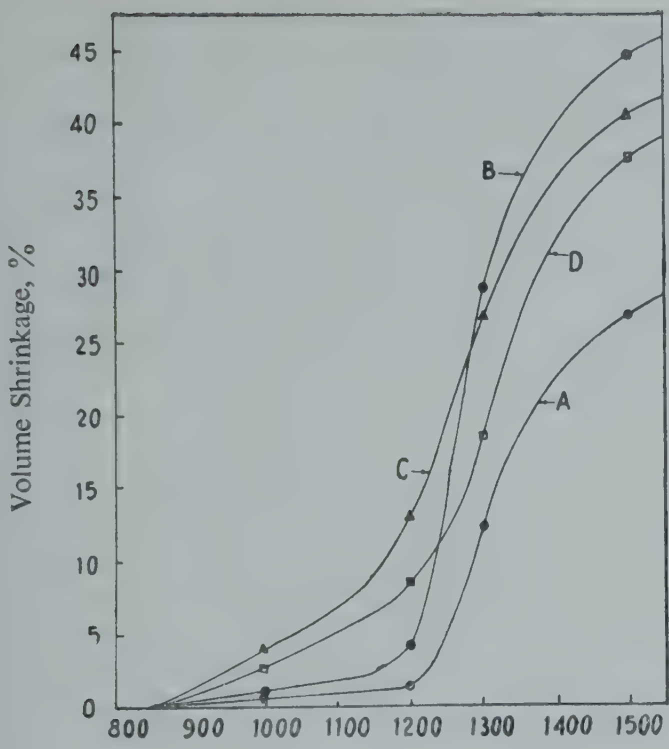

Fig. 1—Volume Shrinkage Vs. Sintering Temperature of Alumina Pellets with or without NiO

A—alumina pellet with 0 p.c. NiO
B—alumina pellet with 2.5 p.c. NiO
C—alumina pellet with 5 p.c. NiO
D—alumina pellet with 10 p.c. NiO

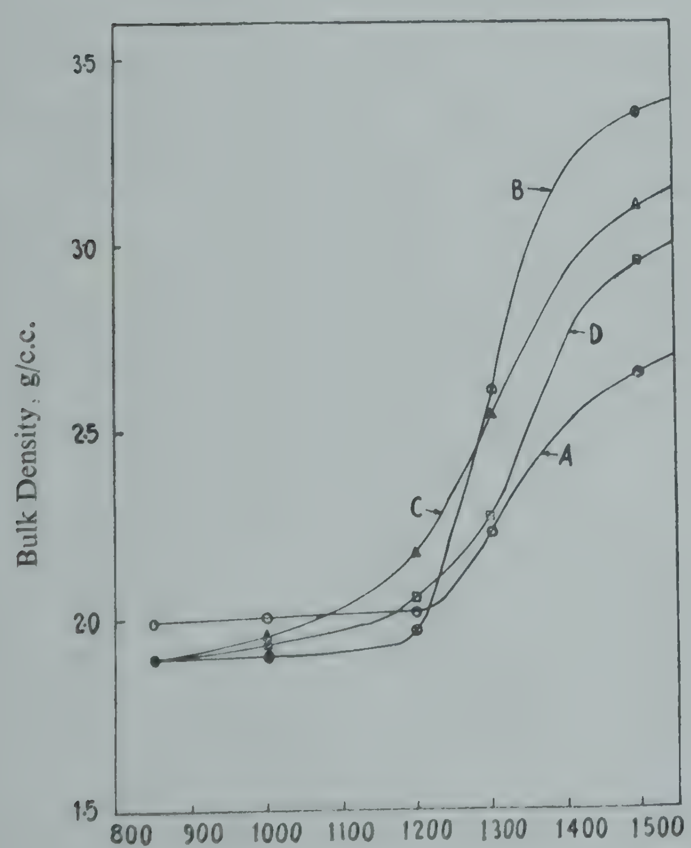

Fig. 2—Bulk Density Vs. Sintering Temperature

A—alumina pellet with 0 p.c. NiO
B—alumina pellet with 2.5 p.c. NiO
C—alumina pellet with 5 p.c. NiO
D—alumina pellet with 10 p.c. NiO

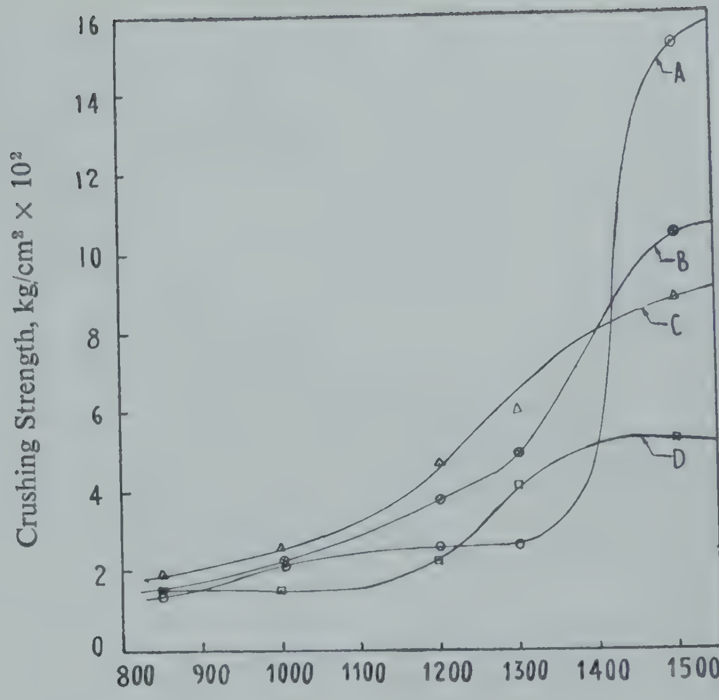

Fig. 3—Crushing Strength Vs. Sintering Temperature

A—alumina pellet with 0 p.c. NiO
B—alumina pellet with 2.5 p.c. NiO
C—alumina pellet with 5 p.c. NiO
D—alumina pellet with 10 p.c. NiO

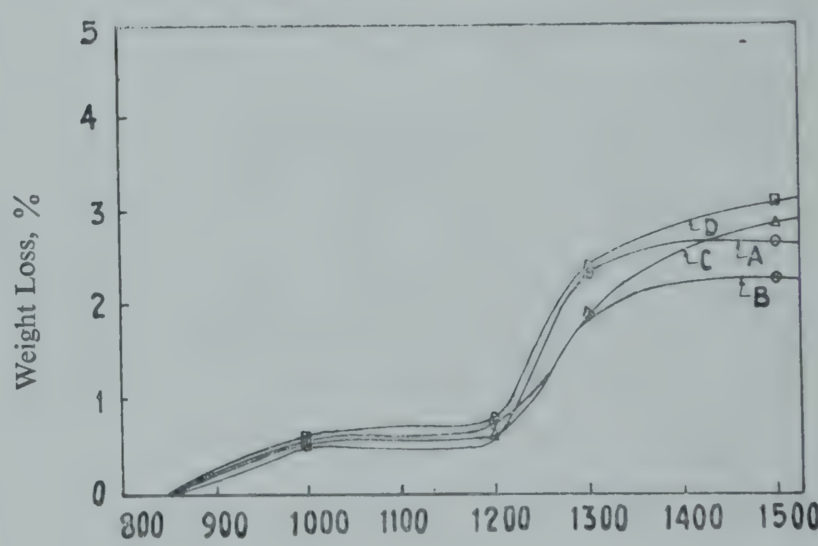

Fig. 4—Weight Loss Vs. Sintering Temperature

A—alumina pellet with 0 p.c. NiO
B—alumina pellet with 2.5 p.c. NiO
C—alumina pellet with 5 p.c. NiO
D—alumina pellet with 10 p.c. NiO

tion. As has been observed by others[2,3] nickel oxide when present in small concentration in an alumina body remains in the grain boundary and inhibits the growth of alumina grains during sintering. It is the smaller grains which favour closer packing during sintering resulting in more densification. With higher nickel oxide content probably spinel ($NiAl_2O_4$) separates out and no nickel is left in the grain boundary of alumina for inhibition of grain growth. It is reported that the shrinkage behaviour

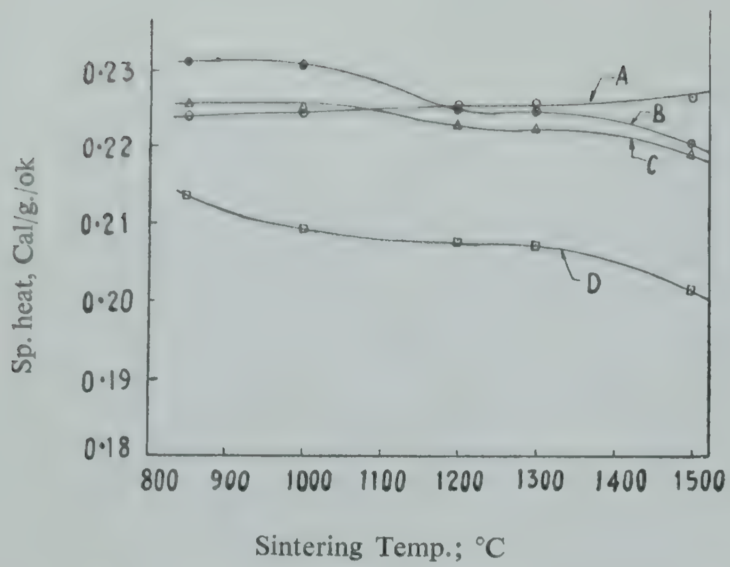

Fig. 5—Specific Heat Vs. Sintering temperature
A—alumina pellet with 0 p.c. NiO
B—alumina pellet with 2.5 p.c. NiO
C—alumina pellet with 5 p.c. NiO
D—alumina pellet with 10 p.c. NiO

of spinel is close to that of pure alumina[1]. So it appears that at 1500°C the much higher densification of the sample containing 2.5 per cent nickel oxide compared to the pure alumina samples and the samples containing 5 and 10 per cent nickel oxide is due to inhibition of grain growth. Less densification of the samples containing 5 and 10 per cent nickel oxide, on the other hand, is probably due to the formation of spinel which is favoured with higher concentrations of nickel oxide in alumina.

Fig. 3 shows that there is a rapid increase of crushing strength of the samples in the same temperature range where shrinkage and densification are maximum. It is interesting to note that the initial crushing strengths of all the samples are very close but the increase in the crushing strength on heat treatment upto 1300°C is more in the case of nickel oxide-bearing samples than that of alumina so that at 1300°C the latter possesses the minimum strength. Again, on heating beyond 1300°C the gain in strength is maximum in case of alumina sample, which attains much higher strength than that of any of the NiO-bearing samples at 1500°C. In fact, above 1300°C, the strength of the samples decreases with increasing concentration of nickel oxide. It is known that the strength and hardness of spinel are less than those of pure sintered alumina[1]. The result, therefore, indicates that spinel formation increases with increasing concentration of nickel oxide which reduces strength progressively on sintering to higher temperatures.

Fig. 5 shows that specific heat is affected both by the sintering temperature and concentration of nickel. While specific heat increases with increasing sintering temperature in the case of alumina the trend is reverse in the case of nickel oxide-bearing samples, the extent of decrease being more prominent at higher temperatures and also when nickel oxide content is more.

It is also observed from Fig. 5 that specific heat decreases with increase of nickel oxide content from 2.5 to 10 per cent at all temperatures of sintering. But it is interesting to note that the specific heat of the alumina sample falls in-between those of the samples containing 5 and 10 per cent nickel oxide, when sintering temperature is below 1000°C. This is probably due to the fact that at lower temperatures of sintering very low concentration of nickel oxide in alumina forms thin film around individual grains and forms no spinel thereby modifying the bulk properties of the alumina in such a way that the specific heat increases. But building up of more and more nickel oxide causes spinel formation thereby decreasing the specific heat. This is more apparent from the fact that at sintering temperatures above 1000°C, where possibility of spinel formation is more, the decrease in specific heat is observed to be more prominent in case of nickel oxide bearing samples.

In the foregoing discussions some light has been thrown on what is happening during the sintering of NiO-Al_2O_3 system. However, better understanding of the sintering mechanism in detail needs studies on sintering kinetics, nature and distribution of grains and crystal phases at different stages of sintering.

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Polarographic behaviour of cupric, ferric and zinc ions in triethanolamine, containing sodium acetate, has been investigated for simultaneous separation of the three ions in a mixture. The base electrolyte, comprising 0.1 M triethanolamine, 0.1 M caustic soda and acetic acid, at pH 8.0 has been found to be ideally suited for the separation of all the three ions. Halfwave potentials of cupric, ferric and zinc ions in this medium were measured to be −0.18 V, −0.45V and −1.12V respectively. These electrode reactions were diffusion-controlled and diffusion currents were found to be dependent on concentration. The system has been applied for the actual analysis of copper, zinc, and iron catalysts used in low temperature CO-conversion. Results have been compared with those obtained by the conventional method of analysis.

Polarographic Study of Copper, Iron and Zinc System in Triethanolamine: Rapid Analysis of Low Temperature CO-Conversion Shift Catalysts

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Introduction

The low temperature CO-conversion catalyst, in general, consists of copper and zinc oxides, usually having the following composition (per cent): copper oxide 30-35, zinc oxide 58-65 and also ferric oxide as a minor constituent 1-2. Its chemical analysis by the conventional methods is time-consuming and laborious. A quick and direct method is essential for its routine analysis required for the development and process control of catalyst production.

The use of polarography for the analysis of similar systems is available in literature. Hohn[1] gave a detailed procedure for the analysis of copper, zinc, nickel and iron in copper-base alloys, using ammonia and ammonium chloride as the base electrolyte. But this method needs a prior separation of iron which is analyzed subsequently. Cozzi[2] recommended a more or less direct method for the simultaneous estimation of trace impurities of iron, copper, bismuth, cadmium and zinc in the refined lead metal using sodium bitartate as a base electrolyte. Souchay and Faucherre[3] used 0.1 M EDTA and 2 M sodium acetate at pH 6-7 for the estimation of small amount of iron in presence of a large excess of copper. However, a polarographic method for the simultaneous estimation of these three ions together is not available in literature.

The present work deals with the simultaneous estimation of the three ions and associated problems. The difficulty in the simultaneous analysis arises due to the fact that both copper and iron produce two waves in most of the commonly used base electrolytes. One of the copper waves in most cases interferes with that of the iron.

Wolfson[4] suggested the use of triethanolamine for the polarographic estimation of iron in 'permalloy'. He reported two waves of iron with $E_{\frac{1}{2}}$ at −0.5 and −1.6V vs SCE in a base electrolyte consisting of 0.3 M triethanolamine; 1.0 M ammonium hydroxide and 0.85 M ammonium chloride. But he found that copper interfered with iron in this medium, so he suggested a preliminary separation of copper. Subsequently, Jessop[5] reported separation of copper, lead, cadmium, iron, nickel and zinc using triethanolamine in conjunction with a strong alkali (0.1 M potassium hydroxide). He noticed that copper, lead and cadmium waves had rounded upper portions in this medium making it difficult to measure the i_d. He also noticed that certain optimum concentrations of triethanolamine and potassium hydroxide are needed to obtain well-defined waves. During preliminary scouting work, the present authors found that zinc did not produce a satisfactory wave in strongly alkaline media in presence of triethnaolamine. It was, therefore, found necessary to re-examine the behaviour of copper,

zinc and iron in triethanolamine and optimize conditions for an effective separation of all the three ions when present together. Jessop[5] also noticed the pH dependence of $E_{\frac{1}{2}}$ of iron in the above supporting electrolyte. Fisher and Hall[6] observed a similarity between the copper-ammonia and copper-triethanolamine complexes, the latter forming a precipitate when concentration of triethanolamine is low which dissolves in excess of the complexing agent. They, therefore, suggested that the amount of triethanolamine needed to keep the complex in a clear solution could be minimized by adding a strong alkali, like caustic soda.

The present investigations were carried out with a base electrolyte consisting of 0.1 M triethanolamine, 0.1 M caustic soda and acetic acid which was used to adjust the pH of the final solutions. This base electrolyte at pH 8.0 was found to be most effective for the separation of all the three ions. The electrode reactions were found to be diffusion-controlled and suitable for quantitative evaluations at this pH. The presence of acetate ions appears to facilitate reduction of copper in a single step.

Experimental

Analytical grade triethanolamine, caustic soda and acetic acid were used for all the experiments. All the polarographic measurements were made by keeping the cell in a thermostatic water-bath at $30°\pm0.1°C$ except for those experiments involving measurement of temperature coefficient of i_d. The d.m.e. used had a drop time of 3.0 sec. and $m^{2/3}t^{1/6}$ was measured to be 2.238 $mg^{2/3}$ $sec^{-1/2}$. All the voltages were measured against SCE.

(1) Different base electrolyte solutions were prepared by mixing triethanolamine and caustic soda such that the final solution had these components in 0.1 M and 0.2 M respectively. pH of these solutions was varied between 5.0 and 12.6 by the addition of acetic acid. The decomposition characteristics of these solutions were observed by running current voltage curves on a Fisher Elecpropode equipped with an 11″ stripchart recorder.

The decomposition potentials of these solutions were measured as shown in the last column of Table 1.

(2) The effect of pH on the $E_{\frac{1}{2}}$ of cupric, ferric and zinc ions in the above base electrolytes was observed by running separate polarograms of the ions between pH 5.0 and 12.6. $E_{\frac{1}{2}}$ for all the waves were measured as shown in Table 1.

(3) In the next series of experiments the effect of pH on the $E_{\frac{1}{2}}$ of these ions was studied in mixtures. $E_{\frac{1}{2}}$ voltages were measured and found to be nearly the same as those for individual ions. From these experiments it was concluded that the most effective separation is obtained at pH 8.0.

TABLE 1—Effect of pH Variation on $E_{\frac{1}{2}}$ of Cu^{2+}, Fe^{3+} and Zn^{2+} at 30°C *vs.* S.C.E. in Base Electrolyte Consisting of 0.1 M Triethanolamine, 0.2 M NaOH and Acetic Acid

[Acetic acid was used to adjust the pH].

pH	$E_{\frac{1}{2}}$ for Cu^{2+}V	$E_{\frac{1}{2}}$ for Fe^{3+}V	$E_{\frac{1}{2}}$ for Zn^{2+}V	Decomposition Potential of the Base, Electrolyte, V
5.0	−0.08	−0.12	−1.110	−1.43
6.0	−0.09	−0.24	−1.115	−1.45
7.0	−0.12	−0.32	−1.120	−1.57
8.0	−0.18	−0.45	−1.125	−1.62
9.0	−0.25	−0.53	−1.130	−1.72
10.0	−0.35	—	—	−1.80

(4) A series of experiments was then carried out to measure the diffusion currents as a function of concentration of copper, zinc and iron ions, the polarograms of which were run individually at pH 8.0. A straight line relationship was obtained when i_d was plotted against concentration for all the three ions.

(5) The temperature coefficient of i_d was measured for all the ions by observing the diffusion currents at pH 8.0 in the range 20.5—32°C. Table 2 shows the temperature effect on the i_d for the various ions.

TABLE 2—Effect of Temperature on i_d

[Diffusion currents measured in 0.1 M triethanolamine, 0.1 M caustic soda and acetic acid to adjust pH to 8.0 The values are ratios of i_d at the indicated temperatures to i_d at 20°C]

Ion	Temperature, °C			Temperature Coefficient, °C
	20	25	30	
Cu^{2+}	1.00	1.13	1.18	1.8
Fe^{3+}	1.00	1.04	1.07	0.7
Zn^{2+}	1.00	1.05	1.10	1.0

(6) The analysis of the three catalyst samples is presented in Table 3. The results are compared with those obtained by the conventional methods. No maximum was observed for any of the ions in the pH range studied so that no maximum suppressor was employed in any of the experiments.

(7) The following procedure was followed for the actual analysis of the catalyst samples: 2.5 g. of catalyst sample

TABLE 3—ANALYSIS OF THREE TYPICAL CATALYSTS BY CONVENTIONAL AND POLAROGRAPHIC METHODS

[The results are on the basis of milligrams of the oxides in solution containing 10 mg. of Catalyst]

Catalyst Sample No.	Polarographic Analysis, mg.			Conventional Method of Analysis, mg.		
	CuO	Fe_2O_3	ZnO	CuO	Fe_2O_3	ZnO
I	3.51	0.171	5.96	3.50	0.167	5.99
II	3.28	0.114	6.49	3.27	0.107	6.46
III	3.10	0.180	6.51	3.11	0.173	6.46

was digested with 25 ml. of 5N nitric acid (C.P.) until dissolution was complete. The solution was evaporated almost to dryness, and redissolved in 150 ml. of distilled water filtered into a 250 ml. volumetric flask and the volume was made up to the mark. 10 ml. of this stock solution was further diluted 10 times in a 100 ml volumetric flask, 10 ml of this solution was taken in a 50 ml. beaker and 5 ml of 1.0 M triethanolamine and 1 ml of 10 M caustic soda were added to it; its pH was then adjusted with 1 M acetic acid to 8, 0 and the volume of this solution was made up to 50 ml. A portion of this solution was transferred to the polarographic cell. The solution was deaerated for 15 min. and polarogram was recorded at $30\pm0.1°C$. Moderate sensitivity was chosen for this polarogram which includes all the three ions. Copper and zinc wave heights were measured from this polarogram. For iron a second polarogram was run on the same solution by compensating the copper current at $E_{d.e} = -0.3V$, using a high sensitivity. The wave height of iron from the second polarogram was measured at -0.6 V for the estimation of iron. Copper, zinc and iron were also estimated from the stock solution by the conventional methods.

Results and Discussion

Copper: Different authors[7–13] have studied the structural aspects of copper triethanolamine complexes. In the present investigation, it was found that the reciprocal slope of the straight line plot for copper between log $\frac{i}{i_d-i}$ *vs* $E_{d.e}$ at pH 8.0 was of the order of 0.04 V indicating that the wave is probably reversible under the conditions employed although the value seems to be higher than what would be expected theoretically for a reversible two-electron charge transfer. However, the copper waves were very well-defined; these waves at pH 8.0 were perfectly suited for quantitative measurements. $E_{\frac{1}{2}}$ of copper waves at various pH values are shown in Table 1. At high pH values the copper waves had a poor shape. 0.1 M triethanolamine was enough to complex the low molarity test ions completely. Best steps for quantitative measurement were obtained in the pH range 7.5 to 8.5. Table 1 also includes results of $E_{\frac{1}{2}}$ variation with pH.

Iron: Iron and copper in a base solution consisting of triethanolamine, ammonia and ammonium chloride produce double waves[4]. One of the copper waves may interfere with the first iron wave in this base electrolyte. Jessop[5] suggested the use of caustic soda instead of ammonia and ammonium chloride in order to prevent this mutual interference. However, the iron wave in this case becomes strongly pH dependent. Polcyn and Shain[14], using a stationary electrode technique, showed that alkaline iron-triethanolamine complexes give two waves, the first being generally reversible and the second appearing close to the decomposition potential of the base electrolyte is irreversible. In the present investigation it was found that upto a pH of about 10, iron reduces giving two waves. Both the waves are well-defined at lower pH values. At higher pH, the second wave overlaps with the reduction of the base electrolyte itself. The first wave of iron at pH 8.0 was found to be suitable for analytical purpose. The slope of the plot of log $\frac{i}{i_d-i}$ *vs* $E_{d.e}$ obtained for the first iron wave was found to be of the order of 0.095 V showing the step to be irreversible at this pH. The ratio of the heights between the second and the first iron waves at pH 8.0 was found to be about 2. Subrahmanya[15] found this ratio to be slightly less than 2. High values of i_d for the second wave of iron could not be used for the measurement of small amounts of iron in the catalyst samples because of this wave's juxtaposition with that of zinc and also because iron wave was measured by the current compensation method. The effect of pH on the $E_{\frac{1}{2}}$ of the iron waves has been shown in Table 1. It can be seen that $E_{\frac{1}{2}}$ of both the waves increases with an increase in pH. Both the waves were found to be well defined between pH 7.5—8.5. It was not possible to measure $E_{\frac{1}{2}}$ above pH 10.0

Zinc: Douheret[7] explained the structure of copper and zinc complex with triethanolamine on the basis of molecular orbital theory using potentiometry and polarographic techniques. Subrahmanya[16] studied the polarographic behaviour of zinc in alkaline triethanolamine solutions and found the zinc waves to be suitable for quantitative estimation of zinc. It was found in the present work that $E_{\frac{1}{2}}$ of Zn^{2+} in the triethanolamine, caustic soda and acetic acid base electrolyte increases with the increase

in pH. At higher pH the waves were not well defined and $E_{\frac{1}{2}}$ could not be measured accurately. These results have been shown in Table 1. Electrode reaction for Zn^{2+} was found to be irreversible. Nevertheless, the wave at pH 8.0 was found to be suitable for analytical purpose. Fig 1. shows the straight line relationship between the i_d values for copper, zinc and iron waves in triethanolamine, caustic soda and acetic acid at pH 8.0. By the treatment of Kolthoff and Lingane[17], the reduction of these three ions under the given conditions appear to be diffusion-controlled. This is further confirmed by the straight line relationship obtained for various concentrations of these ions when plotted against their i_d values (Fig. 2). These plots were obtained by running polarograms of individual ions and measuring their i_d by the absolute method at various concentrations of the ions.

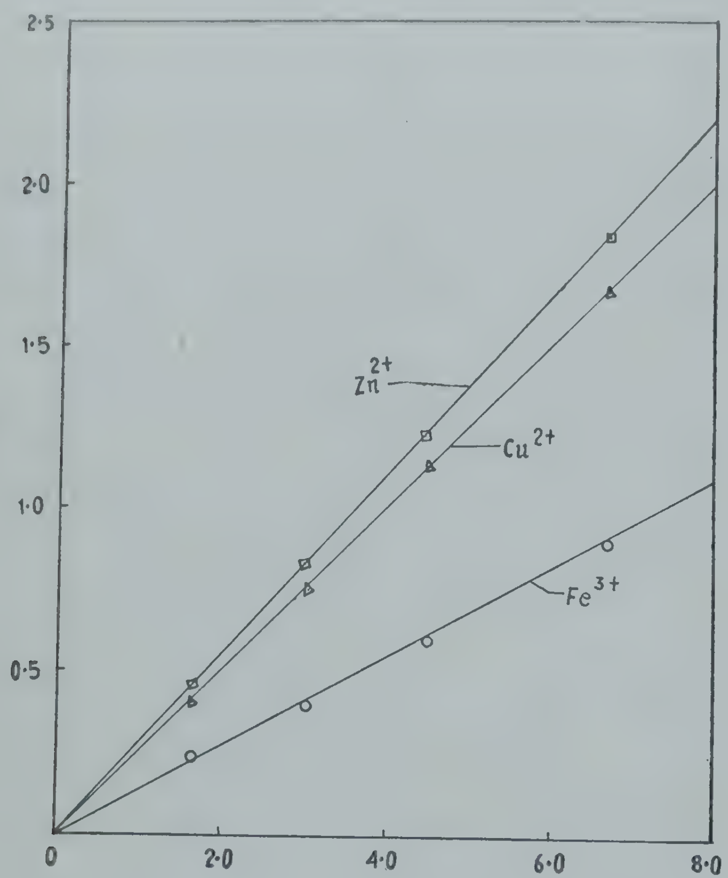

Fig. 1—Effect of Mercury Column Pressure on i_d

For quantitative measurements, cupric, ferric and zinc ion wave heights were measured at $E_{d.e}$ of $-0.3V$, $-0.6V$ and $-1.3V$ respectively. Diffusion current constants i_d were found to be 8.53, 7.93 and 4.09 microamperes/millimole/$mg^{2/3}$ $sec^{1/2}$, respectively at 30°C. A typical polarogram of the three ions present in a mixture is shown in Fig. 3.

The temperature effect on the diffusion current of these ions was studied between 20 and 30°C. (Table 2). The temperature coefficients calculated do not exceed 1.8 per cent/degree and the i_d for ferric ion appears to be least sensitive to temperature variations. This is a desirable feature when measurement of iron involves small concentrations.

Table 3 shows the analysis of three catalyst samples obtained by polarographic as well as the conventional methods. The results are seen to agree well. It is, there-

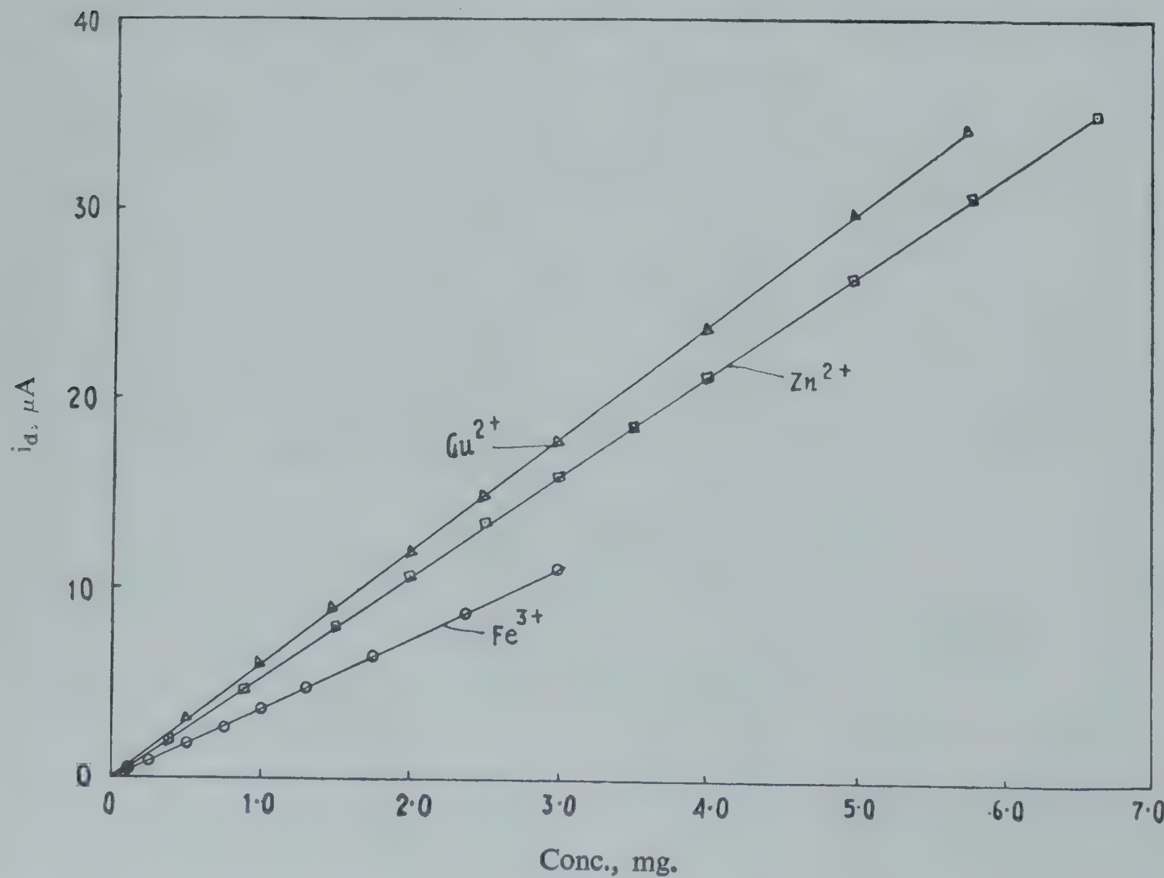

Fig. 2—Concentration Dependence of i_d for Copper, Iron and Zinc in Triethanolamine

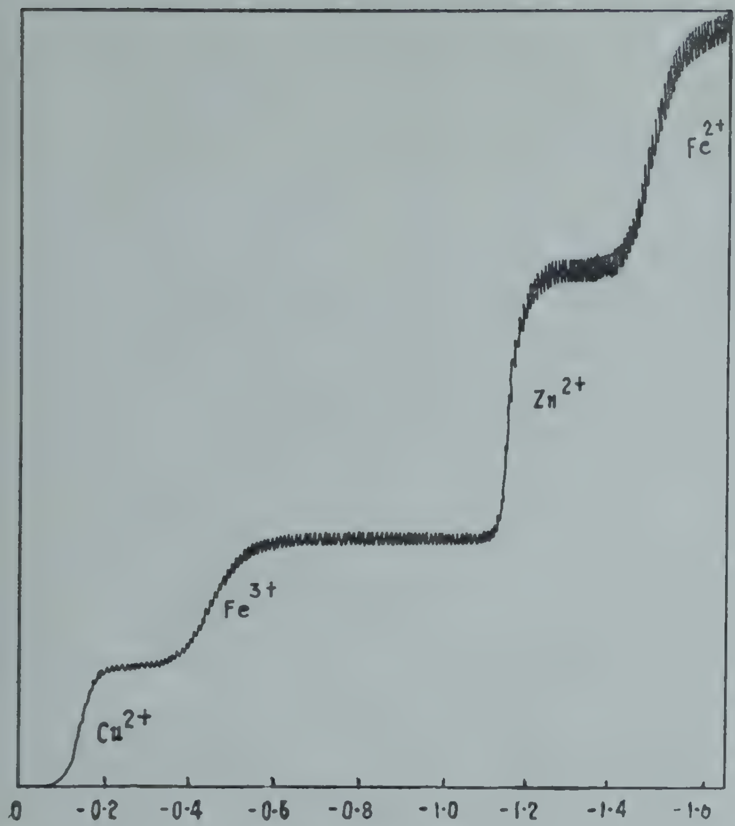

Fig. 3—Typical Polarogram of the Three Ions Present in a Mixture

fore, concluded that well-defined polarographic waves are obtained for copper, iron and zinc ions in triethanolamine containing sodium acetate ions at pH 8.0 This electrolyte system is ideally suited for the rapid simultaneous analysis of these ions when present together in mixture.

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N-bis (β-aminoethyl) dithiocarbamic acid has been used successfully as a reagent for the amperometric titration of selenium (IV) (18.71–3159 ppm) using ammonium acetate-acetic acid mixture as the supporting electrolyte-cum-buffer (pH 4.6). The titrations were carried out at + 0.2 V vs SCE at the rotating platinum micro-electrode and the effect of various interfering ions on this estimation has been studied. The results of the estimation of selenium in pyrites by this method have been shown. The accuracy of the procedure is comparable with that of conventional methods.

Amperometric Complex-Formation Titrations of Traces of Selenium (IV)

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Only a few amperometric titrations are known for the estimation of selenium (IV). Deshmukh *et al*[1] have found that 3 to 38 mg. selenite ion in 0.6 M sodium bicarbonate can be titrated with sodium hypobromite solution to give an average error of about 0.3 per cent. Songina and Voiloshnikova[2] estimated this element by amperometric titration with potassium iodide solution. The reduction of ascorbic acid of selenite and selenate ions in acid solutions giving elementary selenium has been used by Simon and Grim[3] as the basis of an amperometric titration for quantities of from 5 to 30 gm. selenium. The biamperometric titration of selenite with ferricyanide ion was reported almost simultaneously by Deshmukh *et al*[4] and Solymosi[5]. Recently, Deshmukh *et al*[6,7] have reported the estimation of this element with methyldithiobiuret and potassium ethyl xanthate respectively.

In the present study a new amperometric method for the estimation of microgram quantities of this element using N-bis-(β-aminoethyl)-dithiocarbamic acid as the titrant has been described. The method is based on the measurement of the anodic current of the excess titrating agent after the end-point.

Experimental

Reagents: The preparation and standardization of N-bis-(β-aminoethyl) dithiocarbamic acid solution were carried out by the procedures described earlier[8,9]. From E. Merck's reagent, standard solution of sodium selenite was prepared, which was further standardized by the conventional procedure[10]. Ammonium acetate and acetic acid were of AnalaR variety.

Apparatus: Titrations were carried out in an apparatus designed and fabricated in this laboratory[11]. Readings were taken using rotating platinum micro-electrode as polarizable electrode. The non-polarizable electrode used was a saturated calomel electrode with Agar-KCl bridge. pH measurements were made with a Philips pH meter (PR 9403).

Procedure: The titrations of selenium (IV) at the rotating platinum electrode at an applied potential of +0.2V vs SCE were performed in ammonium acetate + acetic acid buffer. The applied potential was so chosen that the metal ion was not reduced but the reagent had its oxidation step at that potential. The following optimum conditions, viz. electrolyte concentration and pH, were established by trial experiments. The final titration procedure adopted in each determination was more or less the same.

An aliquot of the metal ion solution was taken in a 100 ml. pyrex beaker and a requisite amount of ammonium acetate was added to maintain its overall concentration at a desired value in 30 ml. The pH was adjusted with acetic acid. Necessary connections were made and the desired potential was applied. The galvanometer reading was noted initially as well as after each addition of an aliquot of titrant from a 10 ml. microburette. The values of the current were corrected for volume changes by multiplying them with $\frac{V+U}{V}$, where V is the initial

volume of the solution and U, the volume of the titrant added.

Effect of pH: The pH of the medium had a considerable influence on the accuracy of the determination. A pH range 4.2–5.2 was found most suitable for obtaining accurate and reproducible results (Table 1). At other pH value this range, the results were not in agreement with the stoichiometric ratio for the reaction.

Effect of Base Electrolyte Concentration: The overall concentration of base electrolyte was varied from 0.05 to 0.5M maintaining pH at 4.6, when the quantitative results were only between 0.1 and 0.4 M of the base electrolyte (Table 2).

TABLE 1—EFFECT OF pH ON THE AMPEROMETRIC DETERMINATION OF SELENIUM (IV)

[Volume of Solution Titrated 30 ml.]

pH	Selenium (IV), mg.		% Error
	Taken	Found	
4.2	1.00	0.995	−0.50
4.5	1.00	1.005	+0.50
4.6	1.00	1.00	—
4.8	1.00	1.001	+0.10
5.2	1.C0	1.003	+0.30

TABLE 2—EFFECT OF BASE-ELECTROLYTE CONCENTRATION ON AMPEROMETRIC DETERMINATION OF SELENIUM (IV)

[Volume of Solution Titrated 30 ml.]

Base-Electrolyte Concentration (Molar)	Selenium (IV), mg.		% Error
	Taken	Found	
0.1	1.00	1.002	+0.20
0.2	1.00	0.999	−0.10
0.3	1.00	1.001	+0.10
0.4	1.00	1.003	+0.30

The final titrations were carried out in 0.1 M ammonium acetate + acetic acid at pH 4.6 and an applied potential + 0.2 V vs SCE with the rotating platinum microelectrode. The results are recorded in Table 3 (Fig. 1).

Estimation of Selenium in Pyrites: An accurately weighted quantity of the finely powdered sample (20-25 g.) was transferred in a wide-necked conical flask, to which 100 ml. of nitric acid (conc.) was added and then the acid was evaporated to dryness on a water bath. 50 ml. of 2N hydrochloric acid was added and the solution was

TABLE 3—AMPEROMETRIC DETERMINATION OF SELENIUM (IV) WITH N-BIS (β-AMINOETHYL)—DITHIOCARBAMIC ACID

Base-Electrolyte = 0.10 M ammonium acetate + acetic acid, pH = 4.6
Applied potential = +0.2 V vs SCE
Indicator Electrode = Rotating Platinum
Strength of reagent = 1×10^{-2}M
Total volume of the solution = 30 ml.

Curve	Selenium (IV), mg.		% Error
	Taken	Found	
A	0.1	0.099	−1.0
B	0.2	0.201	+0.5
C	0.3	0.300	—
D	0.4	0.402	+0.5
E	0.5	0.498	−0.4

TABLE 4—DETERMINATION OF SELENIUM (IV) IN PYRITES

Sample No.	Selenium in the Sample, ppm.	
	Proposed method	Conventional method
1	21.38	21.00
2	20.05	20.18
3	20.75	21.01
4	21.25	20.87
5	21.12	21.05

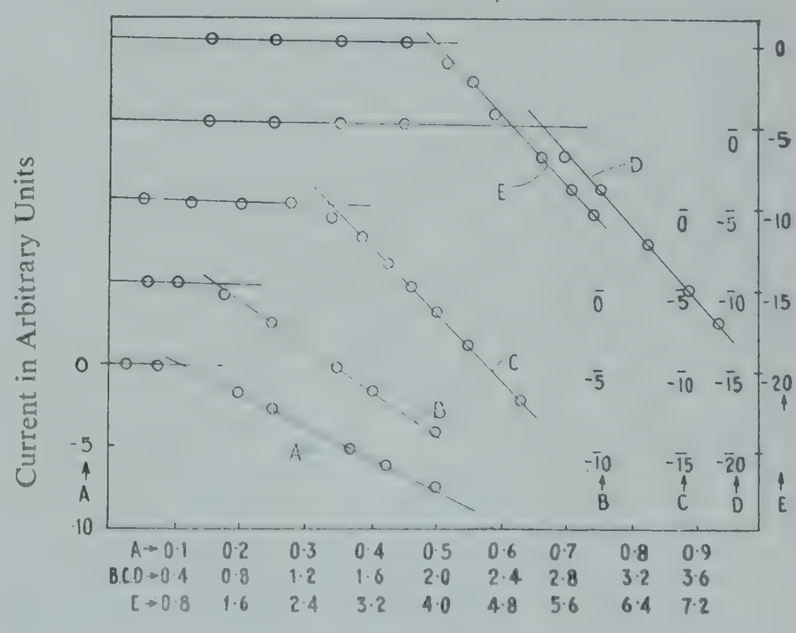

Fig. 1—Amperometric Titration Curve

evaporated to dryness under a reflux condenser. The flask was cooled and 50 ml. of hot water was added to dissolve the salts. The solution was filtered off and the residue washed with hot water. The filtrate diluted to 80

ml, was heated to 40-45°C after adding 40 ml. of hydrochloric acid (conc.). 0.2 g. of potassium iodide, 0.05 g. potassium nitrate were added and the selenium was reduced with a saturated thiourea solution. After 1-1. 5hr. the red precipitate of selenium was filtered off and washed with (x 2 or 3) very dilute hydrochloric acid and then with hot water (x 6 or 7). The precipitate was dissolved in 10 ml. of hydrochloric acid (conc.) and 2 or 3 drops of nitric acid. The solution was made slightly alkaline with liquor ammonia and was diluted to 50 ml. An aliquot of this solution was buffered at pH 4.6 as before and titrated. If the selenium content in the pyrites is too small (<20 ppm), a known amount of selenium may be added to the solution just before reduction with thiourea and the selenium content in the pyrites may be obtained by difference. There are no interferences in this method as separated from the other interfering elements and the agreement with other conventional method[12] is good.

Interferences: 500 ppm of Ce^{4+}, V^{5+}, Zn^{2+}, Mn^{2+}, Sb^{3+}, Sn^{2+}, Co^{2+}, As^{3+}, As^{5+}, Fe^{3+}, Cr^{6+}, and Al^{3+} do not interfere in this determination. The following cations, viz. Pb^{2+}, Ni^{2+}, Cu^{2+}, Bi^{3+}, Mo^{6+}, Cd^{2+}, Ag^{+}, Hg^{2+} and Te^{4+}, were found to interfere.

Results and Discussion

The amperometric titration curves are reverse L shaped, with a sharp break at the end-point which occurs at a stage when metal: reagent ratio is 1:4. The useful range for the estimation of this element has been found to be between 2.5×10^{-3} and $4.22\times10M^{-5}$ (3159–18.71 ppm) with respect to the metal ion in the solution. The procedure is very rapid as each determination requires only 3-4 minutes. From the observed results it has been seen that the complex has the formula $(C_5H_{13}N_3S_2)_4Se$.

Campbell and Reilley[13] and Freese *et al*[14] have described the amperometric titration of milligram amounts of metal ions with chelating agents such as EDTA and Trien, the end-point being detected by means of the anodic wave of the chelating agent. The theory of the anodic amperometry can be explained as follows:

The titration of a cation M with a ligand Y by the reaction $M+Y = MY$ is very sharp in the microgram range, i.e. the degree of titration, expressed as a function of the free ligand concentration (Y), shows a sharp break at the equivalence point. The necessary condition may be derived easily. If the total amount of metal and ligand present in the system are denoted by C_M and C_Y respectively, then

$$C_Y = [Y]+[MY] \text{ and } C_M = [M]+[MY].$$

Combining these equations with

$$K = \frac{[MY]}{[M]\,[Y]}$$

we obtain,

$$\frac{C_Y}{C_M} = \frac{[Y]+[MY]}{C_M} = \lambda$$

$$= \frac{[Y]}{C_M} + \frac{[MY]}{[M]+[MY]}$$

$$= \frac{[Y]}{C_M} + \frac{K[M]\quad[Y]}{[M]+K\,[M]\,[Y]}$$

$$= \frac{Y}{C_M} + \frac{K\,[Y]}{1+K[Y]}$$

$$= \lambda_O + \lambda_K$$

which simplifies to

$$\lambda = \frac{[Y]}{C_M} + 1$$

for a sharp titration after the equivalence point. The titration curve, as a function of [Y], can be derived by adding two terms λC (dependent only on C_M) and λ_K (dependent only on K). For a sharp titration there will be a linear rise in [Y] after the equivalence point and hence a linear rise in the anodic current.

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Phosphorus pentasulphide has been successfully used as a reagent for the amperometric titration of traces of trivalent arsenic (3.32 to 100 ppm.) using ammonium acetate-acetic acid mixture as the supporting electrolyte-cum-buffer (pH 4.5). The titrations were carried out at 0.0 V vs SCE using the rotating platinum micro-electrode and the effect of various interfering ions has been studied. This procedure has been utilized to estimate trace quantities of arsenic in fertilizers. Titrations were carried out using an apparatus designed and fabricated in this laboratory. This procedure is comparable with the conventional methods for accuracy.

Amperometric Determination of Trivalent Arsenic with Phosphorus Pentasulphide

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Very small amounts of arsenic (0.001-0.1 mg.) may be determined by the Gutziet test. Although this method is adopted by the Sindri Unit, FCI Ltd. for estimating small amounts of arsenic in fertilizers, it is doubtful whether the accuracy exceeds ten per cent of the true value. Therefore, a suitable reproducible method was very much required for the estimation of arsenic in fertilizers. The present paper is an attempt towards the same.

So far only a few amperometric titration procedures are known for the estimation of trivalent arsenic. Laitinen and Kolthoff[1] first used potassium bromate in amperometric titration of arsenic trioxide in a solution containing 1.0 M hydrochloric acid in 0.05 M potassium bromide. Harris and Lindsey[2] have titrated 0.001 N sodium arsenite solutions with a standard iodine solution, a reverse L-type of titration graph being produced. Zuman and Zumanova[3] titrated it amperometrically with 2.3 dimercapto propanol. Zodanov *et al*[4] have reported that iodine monochloride can be used to titrate arsenic (III) in a saturated sodium bicarbonate solution or in 0.3 M sodium phosphate. Kolthoff *et al*[5] titrated arsenic (III) solution with sodium hypobromite solution in 0.2M sodium bicarbonate buffer at a rotating platinum electrode of potential +0.2V vs SCE. In the present investigation, a new amperometric procedure for the estimation of trace quantities of this element with phosphorus pentasulphide as the titrant has been developed.

Polarographic characteristics of the phosphorus pentasulphide showed an irreversible anodic wave over a wide span of applied potential (—O.7 V vs SCE) in various electrolytes, such as ammonium acetate + acetic acid, ammonium acetate + ammonia, sodium tartarate + sodium hydroxide and ammonium nitrate + ammonium hydroxide in the pH range 3.8–12.0. In 0.5 M ammonium acetate + acetic acid buffer (pH 4.5) the $E_{\frac{1}{2}}$ of the anodic wave of phosphorus pentasulphide was found to be −0.35 V vs SCE. The half-wave potential shifted to more negative values with increasing alkalinity of the solution and at the same time a slight increase in diffusion current was observed. However, the well-defined nature of the wave was unaffected with increasing alkalinity of the solution. The constancy of $i_d/\sqrt{h_{Hg}}$ values indicated that the waves are diffusion-controlled. This anodic wave results either from the oxidation of phosphorus pentasulphide or from the interaction of phosphorus pentasulphide and oxidized mercury rather than from an oxidation of phosphorus pentasulphide[6]. The probable oxidation products may be sulphate and phosphate respectively in the solution. The diffusion current was found to be proportional to the concentrations. This has been utilized for developing an amperometric titration method for the estimation of arsenic (III). The applied potential is so chosen that arsenic (III) is not reduced[7] but the reagent had its oxidation step at that potential. As long as the precipitate occurred the current readings remained steady and after the end-point the anodic current of the excess reagent increased. In the graphical representation of data, the intersection of the two linear portions with the volume axis corresponds to the end-point of the titration.

EXPERIMENTAL

Reagents

(1) *Arsenic* (III) *Solution*: E. Merck's guaranteed arsenious oxide was employed. An accurately weighed quantity of the sample was dissolved in 1N aqueous sodium hydroxide. The pH of this solution was adjusted to 7.0 with hydrochloric acid (dil) and its strength was checked by the conventional procedure.[8]

(2) *Phosphorus Pentasulphide Solution*: 0.01M stock solution of phosphorus pentasulphide was prepared by dissolving an accurately weighed quantity of the E. Merck's guaranteed sample in ammonium hydroxide solution. The pH was adjusted to 7.5 with acetic acid. This solution was further standardized by the procedure described earlier.[9] Ammonium acetate, acetic acid and other reagents were of AnalaR quality.

Equipments

Titrations were carried out with the rotating platinum microelectrode, for which a compact manual amperometric unit, complete with a potentiometer and a suitable spot reflecting galvanometer as a current-measuring device[5] was set up. A schematic diagram of the apparatus is shown in Fig. 1. An automatic recording Cambridge

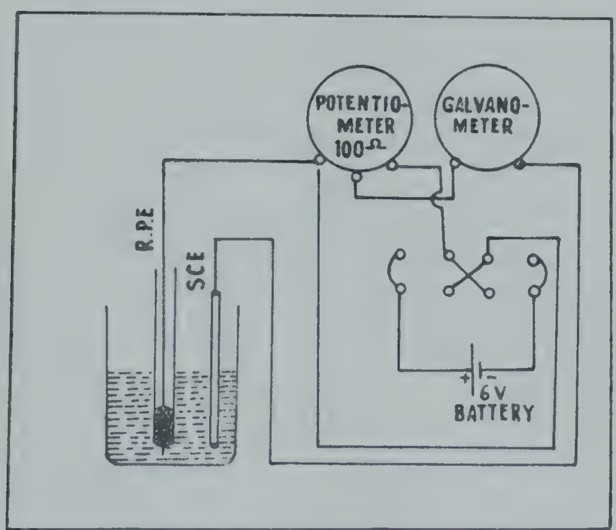


Fig. 1—A Schematic Diagram of the Apparatus

Univector Polarograph (using D.C. polarography) with a dropping mercury electrode was used to obtain necessary polarographic data. The characteristics of the dropping-mercury electrode were m = 1.042 mg/sec, t = 4.4 sec. The non-polarizable reference electrode used was a saturated calomel electrode with Agar-KCl bridge. pH measurements were made with a Philips pH-meter (PR 9403).

Procedure

The titrations were carried out at an applied potential of 0.0 V vs SCE using ammonium acetate + acetic acid as buffer and after establishing the optimum condition, viz. base electrolyte concentration and pH by trial experiments. The procedures adopted in each determination were more or less the same. An aliquot of the arsenic (III) solution was taken in a 100 ml. pyrex beaker and the requisite amount of ammonium acetate was added to maintain its overall concentration at the desired value in 30 ml. The pH of the solution was adjusted with acetic acid. Necessary connections were made and the desired potential was applied. The galvanometer reading was noted initially as well as after each addition of an aliquot of titrant from a calibrated 10 ml. microburette (graduated in 0.01 ml.).

Effect of pH: The variation of the pH of the medium influences considerably the stoichiometry of the reaction. A series of amperometric titrations were carried out with 0.10 M ammonium acetate, adjusting the pH to the desired values with acetic acid. The same known quantity of arsenic (III) was used in each case. Accurate and reproducible results were obtained at pH between 4.2 and 5.0; at other values below and above this range, the results were not in agreement with the stoichiometric ratio for the reaction (Table 1).

Effect of Base-Electrolyte Concentration: With the overall concentration of base electrolyte varying from 0.02 to 0.15 M at pH 4.5, the limit of concentration of the titre values remains unaffected (Table 2).

TABLE 1—EFFECT OF pH ON AMPEROMETRIC DETERMINATION OF ARSENIC (III) WITH PHOSPHORUS PENTASULPHIDE

pH	Arsenic (III)		Error, %
	Taken, mg.	Found, mg.	
4.2	1.00	0.999	−0.10
4.5	1.00	1.00	—
4.8	1.00	1.002	+0.20
5.0	1.00	1.002	+0.20

TABLE 2—EFFECT OF BASE ELECTROLYTE CONCENTRATION ON AMPEROMETRIC DETERMINATION OF ARSENIC (III) WITH PHOSPHORUS PENTASULPHIDE

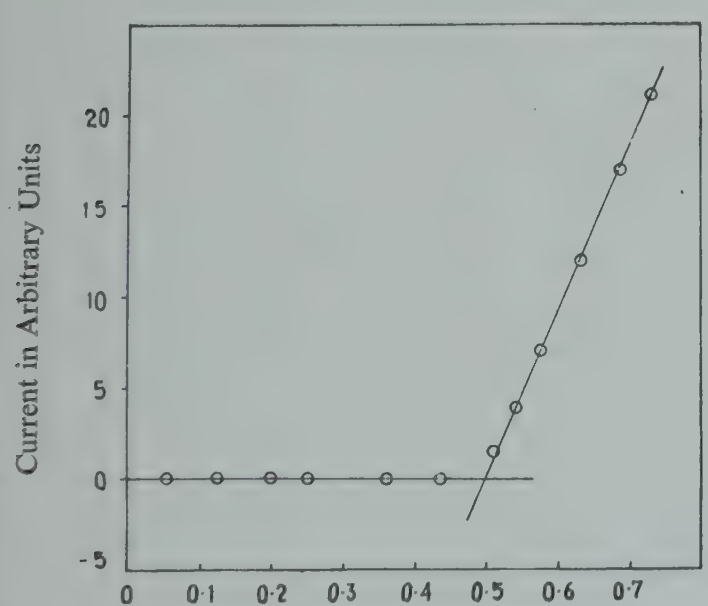
Base-Electrolyte Concentration, M	Arsenic (III)		Error, %
	Taken, mg.	Found, mg.	
0.02	1.00	0.995	−0.50
0.05	1.00	1.001	+0.10
0.10	1.00	1.002	+0.20
0.15	1.00	1.002	+0.20

Final titrations were carried out in 0.10 M ammonium acetate + acetic acid at pH 4.5 at an applied potential of 0.0 V vs SCE. with the rotating platinum micro-electrode (Table 3). A typical amperometric titration curve is shown in Fig. 2.

TABLE 3—AMPEROMETRIC DETERMINATION OF ARSENIC (III) WITH PHOSPHORUS PENTASULPHIDE

Basic Electrolyte = 0.10 M Ammonium Acetate + Acetic Acid, pH = 4.5
Applied Potential = 0. 0 V vs SCE.
Indicator Electrode = Rotating Platinum
Strength of Phosphorus Pentasulphide = 0.01 M

Serial No.	Arsenic (III)		Difference, ppm.
	Taken, ppm.	Found, ppm.	
1.	3.32	3.31	−0.01
2.	16.60	16.60	0.00
3.	33.21	33.20	−0.01
4.	66.42	66.43	+0.01
5.	99.60	99.62	+0.02



Titrant Added, ml.

Fig. 2—A Typical Amperometric Titration Curve

Interferences: The following cations, viz. Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Bi^{3+}, Pb^{2+}, Cd^{2+}, Fe^{3+}, Sn^{2+}, Ag^{+}, Hg^{2+}, Se^{4+}, Te^{4+}, Mo^{6+} and Cr^{6+}, were found to interfere in the estimation of arsenic (III) with phosphorus pentasulphide. The interferences due to the presence of the following cations, viz. Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Bi^{3+}, Pb^{2+}, Cd^{2+} and Fe^{3+} can easily be masked by adding a slightly excess than the theoretical value of EDTA in the system.

Analytical Application: The estimation of arsenic in commercial ammonium sulphate is important because of its poisonous behaviour towards crops. This procedure was adopted in estimating traces of arsenic in ammonium sulphate manufactured at FCI Ltd. Sindri Unit. Eight samples were analysed and the results compared with those obtained by molybdenum blue method[8] (Table 4). In the actual procedure, 10 g. of the sample was weighed accurately in a clean beaker. 20 ml. of 0.2 M ammonium acetate, 0.2 g. of EDTA and 0.2 g of hydrazine sulphate were added and the pH of the solution was adjusted at 4.5. The contents were diluted to 40 ml. and the titrations were carried out at 0.0 V vs SCE.

TABLE 4—DETERMINATION OF ARSENIC IN COMMERCIAL AMMONIUM SULPHATE

Sample No.	Arsenic Found by Amperometric Method, ppm.	Arsenic Found by Molybdenum Blue Method, ppm.
1.	35.1	35.00
2.	40.05	40.00
3.	60.00	60.10
4.	60.00	60.00
5.	65.03	65.00
6.	70.01	70.05
7.	75.00	75.00
8.	80.01	80.01

Results and Discussion

The amperometric titration curves are reverse L-shaped; a sharp break is obtained at the end-point which occurs at the stage when As III: P_2S_5 ratio is 1:1. This method of estimation of arsenic (III) is a precipitation titration of arsenic with sulphide ions generated from phosphorus pentasulphide. Phosphorus pentasulphide hydrolyzes in acid, water or alkali to give predominantly hydrogen sulphide and phosphoric acid according to the equation:

$$P_2S_5 + 8H_2O \rightarrow 2H_3PO_4 + 5H_2S$$

Presumably, there are a number of intermediates which have not been isolated[10]. Since the above equation is also valid at pH 4.5, at which the titrations were carried out, the mechanism of the precipitation can be explained as follows:

$$P_2S_5+8H_2O \rightarrow 2H_3PO_4+5H_2S \quad (X3) \qquad (1)$$

$$2NaAsO_2 + 3H_2S + 2CH_3COOH \rightarrow As_2S_3 + 2CH_3COONa + 4H_2O \quad (X5) \qquad (2)$$

Adding (1) and (2) we get

$$10NaAsO_2 + 3P_2S_5 + 10CH_3\,COOH + 4H_2O \rightarrow 6H_3PO_4 + 5As_2S_3 + 10\,CH_3\,COONa.$$

The data in Table 3 are reproducible and within limits of experimental errors. The procedure is very rapid as each determination requires only 3-4 min. It may be pointed out that the method is comparable with other conventional procedures in so far as its simplicity and precision are concerned. The possibility of applying this technique to the estimation of other cations, either individually or in their binary mixtures, has been envisaged to widen the utility of phosphorus pentasulphide as a potential reagent in electrometric titration. Indeed, it may be well claimed that the delineation of the operative conditions, through a series of trial experiments, to introduce and also to widen the scope of this reagent as a titrant in amperometry is perhaps the most noteworthy feature of this technique.

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There is an appreciable amount of native-fixed ammonium nitrogen in most of the Indian soils. The effect of ionizing radiation on the above ammonium nitrogen of six different soils having different pH has been assessed in this paper. The release of ammonium nitrogen by irradiation has been noticeable, which is not dependent on the texture and organic matter content of the soil; however, the clay minerals in the soil play a dominant role in the above reaction. Soils having illitic-type clay mineral show the highest native-fixed ammonia content, followed by those having kaolinitic type and the lowest has been observed in soils with montmorillonite-type clay. Further, an increase in the exchangeable ammonium nitrogen, besides the amount released from the native-fixed ammonium nitrogen in the irradiated soil, has been attributed to the pH of the original soil.

Native-Fixed Ammonium Nitrogen in Different Indian Soils and the Effect of Ionizing Radiation on it

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Investigation on the native-fixed ammonium nitrogen contents in soils has been carried out by various schools of workers,[1–3] from various angles. But none of them could categorize its state of existence in the soil complex. The soils, varying both in pH and clay minerals content, have obviously different ammonium nitrogen fixed in them. 14 to 78 per cent of the total nitrogen in tropical soils[4] are found to be present in the fixed form. An average of about 2.3 m.e. of fixed ammonium/100 g. of soils is equivalent to about 600 lbs. of nitrogen/acre and it would have been an important source of nitrogen provided it can be made available to crops.

A few workers[5–6] have studied the effect of ionizing radiation in releasing nitrogen to crops. However, conflicting results about the variation in exchangeable ammonium and nitrate nitrogen contents in soils after irradiation have been reported. No one has so far reported any change in the native fixed ammonium content in soils due to irradiation. But it has been confirmed by Bowen *et al*[7] that crops grown in irradiated soils give better yield; they found a consistent change in the total exchangeable nitrogen content in soils due to irradiation.

Keeping this in view, it was thought necessary to assess the native fixed ammonium content of different Indian soils varying in texture, pH and type of clay minerals present and also to study the effect of ionizing radiation on the native fixed and exchangeable ammonium contents of these soils.

Experimental

Materials and Methods: The soils were collected from the following locations: (1) Dinhata (W. Bengal), (2) Netarhat upland (Bihar), (3) Ranchi lowland (Bihar), (4) Barrackpore (W. Bengal), (5) Gwalior (M.P.) and (6) Amroati (Maharashtra). Their physico-chemical properties are given in Table 1.

Gamma Irradiation of Soils: 50 g. of each of the above soils (air-dried), previously ground and passed through 2 mm. sieve (BSS), were taken in a 50 c.c. beaker. These were placed in the gamma chamber having a 2.5 kilo Curie γ source giving a dose of 0.5 mega rad/hr. The soils were irradiated for 48 hours continuously.

The samples of pure montmorillonite and illite clays, supplied by Ward's Natural Science Establishment Inc. New York, were powdered and passed through 100 mesh sieve (BSS). These clays were treated with diammonium-phosphate and ammonium chloride separately giving a dose of 0.9 g. ammonium nitrogen and kept for 24 hours with intermittent shaking. These treated clays were then washed several times with water and 35 per cent alcohol to remove the free ammonium ions. These were then dried in an oven at 70°C for 6 hours, powdered and

TABLE 1—PHYSICO-CHEMICAL CHARACTERISTICS OF VARIOUS SOILS

Location of Soils	Texture	Clay, %	Type of Clay Minerals Present	Organic Carbon (Walkley and Black's value), %	Total N, %	pH Soil: Water (1:2.5)
Dinhata Soil (0-6″ Surface Soil)	Alluvial Silty loam	14	mainly illite	0.60	0.11	4.5
Netarhat upland soil (0-6″ surface soil)	Clay	61	mainly kaolinite	0.35	0.08	5.3
Ranchi low land soil (0-6″ surface soil)	Clay loam	47	mainly kaolinite	0.62	0.09	5.9
Barrackpore soil (0-6″ surface soil)	Alluvial Sandy loam	12	mainly illite	0.48	0.09	7.0
Gwalior soil (0-6″ surface soil)	Alluvial Sandy loam	14	mainly illite	0.36	0.07	8.1
Amroati soil (0-6″ surface soil)	Black loam	50	mainly montmorillonite	0.35	0.08	8.4

passed again through 100 mesh. A portion of each of these treated clays were irradiated in the chamber according to the above procedure.

Native fixed ammonium content of the above irradiated and non-irradiated soils and also ammonium nitrogen treated pure illite and montmorillonite clays were determined according to Dhariwal and Stevenson's[8] procedure, in which the soils and clays were pretreated by autoclaving for 10 hours in potassium hydroxide (N) medium and leaching with potassium chloride (N), before treatment with normal hydrofluoric: hydrochloric acids.

The exchangeable ammonium nitrogen of both irradiated and non-irradiated soils were done by leaching the soil with sodium chloride (N) at pH 2.5 The leachate collected was distilled for ammonia with magnesium oxide and absorbing it in excess acid.

The ammonium nitrogen in both these distillates were determined colorimetrically using Nessler's reagent.

Results and Discussion

The native-fixed and exchangeable ammonium contents of different Indian soils and treated clays, before and after irradiation, are presented in Tables 2 and 3.

It is clearly observed that almost all the soils studied contain appreciable quantities of the native fixed ammonium ions. Dinhata, Gwalior and Barrackpore soils show high native-fixed ammonium, followed by Netarhat and Ranchi soils, while the lowest is observed in Amroati soil.

All the samples except Amraoti soil after irradiation show noticeable changes in the native-fixed as well as exchangeable ammonium contents. It is also observed

TABLE 2—NATIVE-FIXED AND EXCHANGEABLE AMMONIUM NITROGEN CONTENT OF SOILS BEFORE AND AFTER IRRADIATION

Location of Soil	Native-fixed NH^+_4-N, m.e./100 g.			Native-fixed NH^+_4-N, % of Total N	Exchangeable NH^+_4-N, m.e./100 g. soil		
	Non-irradiated i.e. original soil (1st Stage)	Irradiated Soil (2nd Stage)	NH_4^+-N, Released after irradiation		Non-irradiated i.e. original soil (1st Stage)	Irradiated soil (2nd Stage)	Exchangeable NH^+_4-N released after irradiation
Dinhata	1.55	1.55	Nil	19.7	0.85	0.87	0.02
Netarhat upland	1.30	1.20	0.10	22.8	1.35	1.55	0.20
Ranchi lowland	1.20	1.10	0.10	18.6	1.03	1.20	0.17
Barrackpore	1.45	1.35	0.10	22.6	0.70	0.80	0.10
Gwalior	1.50	1.40	0.10	30.0	0.70	0.80	0.10
Amroati	0.80	0.80	Nil	14.0	1.20	1.20	Nil

C.D. at 5%
of Place means = 0.01
„ Stage „ = 0.006
„ Place × Stage „ = 0.014

C.D. at 5%
of Place means = 0.01
„ Stage „ = 0.01
„ Place × Stage „ = 0.016

TABLE 3—NATIVE-FIXED AND EXCHANGEABLE AMMONIUM NITROGEN CONTENT OF DIFFERENT FERTILIZER-TREATED CLAY MINERALS BEFORE AND AFTER IRRADIATION

Type of Clay Minerals	Native-fixed NH^+_4-N, m.e./100 g. clay						Exchangeable NH^+_4-N, m.e./100 g. clay					
	Clay-Treated with NH_4Cl			Clay Treated with $(NH_4)_2$ HPO_4			Clay Treated with NH_4Cl			Clay Treated with $(NH_4)_2$ HPO_4		
	Before Irradiation	After Irradiation	NH^+_4-N Released After Irridation	Before Irradiation	After Irradiation	NH^+_4-N Released After Irridation	Before Irradiation	After Irradiation	NH^+_4-N Released After Irridation	Before Irradiation	After Irradiation	NH^+_4-N Released After Irridation
Illite	7.3	6.9	0.4	7.0	6.6	0.4	11.0	11.4	0.4	14.0	14.6	0.6
Montmorillonite	3.0	3.0	Nil	3.0	3.0	Nil	68.8	68.8	Nil	73.8	73.8	Nil

C.D. at 5% level of type means — 0.03
C.D. at 5% level of stage means — 0.05
C.D. at 5% level of type × stage means — 0.07

C.D. at 5% level of type means — 0.04
C.D. at 5% level of stage means — 0.06
C.D. at 5% level of type × stage means — 0.08

that the change in exchangeable ammonia in soils after irradiation is more in soils having lower pH.

From Table 3, it can be seen that ammonium nitrogen treated illite and montmorillonite clays show much difference in native-fixed and exchangeable ammonium contents and this difference is also noticeable with the change in the type of fertilizers and irradiation. Illite clay shows highest native fixed ammonium content compared to montmorillonite irrespective of the fertilizer treatment. Irriadiation of the ammonium nitrogen-treated clays shows appreciable changes in the native-fixed ammonium content only in the case of illite and a simultaneous change in the total exchangeable ammonium nitrogen is also observed, while montmorillonite does not show any change. Such changes in illite clay are observed more, when it is treated with diammonium phosphate than with ammonium chloride.

An evaluation of the native-fixed ammonium percentage of total nitrogen (Table 2) shows that most of the soils of different texture and pH are having almost similar values except those of Gwalior and Amroati. Gwalior soil shows the highest percentage (30 per cent) fixed as native-fixed while the Amroati soil is lowest (14 per cent).

Comparing the native-fixed ammonium content of the soils and the nature of clay minerals present, an interdependence between the two is quite noticeable. The soils having illite type of clay mineral show the highest native fixed ammonium content, followed by those containing the kaolinite type, while the lowest is observed in those having the montmorillonite type. There is a variation in native-fixed ammonium content in soils containing the same type of clay minerals which may be due to variation in the amount of clay minerals present.

Mikami *et al*[9] reported that soils having high native fixed ammonium are dominated by kaolinite and mica. As clay minerals play a dominant role in the fixation of ammonium content in soils, an interdependence between the two is quite probable. Most of the soils, excepting Amraoti soil, after irradiation show some release of native fixed ammonium, and a simultaneous increase in the exchangeable ammonium content is also noticeable. This indicates that the ammonium ions, which were present in the clays of illitic and kaolinitic types in a difficultly or, rarely exchangeable form, through the replacement of cations, are released probably due to irradiation and are found as an exchangeable ion (extracted normal sodium chloride at pH 2.5) in the irradiated soils. In this context it is worthwhile to mention here, that the x-ray diffraction pattern of the clay samples before and after irradiation showed the changes in the structural characteristics of ammonium fertilizers treated illite after irradiation by the way of displacement of 'd' spacings in the 002 place and the variation of relative intensity in 004, 006, 008, 0010 planes (unpublished work). Ammonium fertilizers-treated montmorillonite after irradiation did not exhibit such changes by the way of displacement or, the variation in relative intensity amongst the planes.

It is known[10] that the phosphate ions facilitate the ammonium ion to remain in a difficultly exchangeable

form in soil treated with ammonium phosphate. It is clear, therefore, that the ammonium phosphate-treated illite clays release more ammonium ion after irradiation than the ammonium chloride-treated illite clays, because irradiation changes the difficultly exchangeable ammonium ion into an easily exchangeable form.

A closer scrutiny of the results of the exchangeable ammonium present in soils before and after irradiation (Table 2) show that organic matter does not play much part in releasing nitrogen from it in an exchangeable form. Again, it is seen that the soils having pH less than 7.0 (i.e. Ranchi lowland, Netarhat upland and Dinhata soils) show increasing exchangeable ammonium ion (besides the ammonium ion liberated from the native-fixed ammonium content) after irradiation with the decreasing soil pH, whereas it does not increase in soils having pH 7.0 or more (i.e. Barrackpore, Gwalior and Amroati soils).

One pertinent point which requires consideration is that the total exchangeable ammonium ion of each irradiated and non-irradiated soils is partly dependent on the ammonifying bacteria and partly on the nitrifying bacteria present in the soil, nevertheless the contribution of the released native fixed ammonium ion due to irradiation is a major factor. It is known that enzymes, including urease, are generally active in the acidic soils, whereas the nitrifying bacteria are active in the alkaline soils. McLaren *et al*[11] observed that the enzymes, including urease, which produces ammonia as a decomposition product, are not inactivated in irradiated soils, whereas the nitrifying bacteria are killed by irradiation. This may account for the increased exchangeable ammonia (besides the ammonium ion liberated the native fixed) in the acid soils after irradiation. This increase is observed upto pH 5.3 after which it diminishes as is observed in the Dinhata soil (pH 4.5). The soils having higher pH are dominated by the nitrifying bacteria, which are killed due to irradiation, and subsequently show no change in the exchangeable ammonium content besides the one liberated from native-fixed ammonium.

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An allowed electronic transition of benzenoid origin has been investigated in each of 2,5-: 2,6- and 3,4- dichlorostyrenes. The vapours of 2,5- and 3,4- dichlorostyrenes exhibit weak discrete absorption in the region $\lambda\lambda$ (3100-2950) and $\lambda\lambda$ (3040-2890) respectively, while a faint continuum, centered at about λ (3050) has been observed in the case of 2,6- dichlorostyrene. The infrared spectra of these compounds have also been obtained in the frequency range 250-4000 cm^{-1}. The 0,0 transitions and the vibrational analyses have been proposed, and the mode of vibrations discussed. The vibronic diffuseness in the electronic transitions has been accounted in term of steric interaction between the chlorine atoms and the vinyl group.

Electronic and Vibrational Spectra of 2,5-, 2,6- and 3,4-Dichlorostyrenes

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It is well established that the longest wave length system of styrene molecule[1–4] pertains to an allowed transition, $A' \leftarrow A'$ of benzenoid origin, $B_{2u} \leftarrow A_{1g}$. Recently, the electronic and vibrational spectra of some substituted styrenes[5–13] were reported. It has been seen that the conjugation of two chromophors, namely vinyl and phenyl groups, affects remarkably the styrene states, the redistribution of the vibronic intensity and the geometry (deviation from coplanarity in excited state). Further, to extend such studies, the electronic and vibrational spectra of 2,5-; 2,6-and 3,4-dichlorostyrenes (heretoafter referred as 2,5-DCS; 2,6-DCS and 3,4-DCS respectively) were investigated. In this paper similar spectroscopic data have been presented and discussed.

As regards the earlier spectroscopic observations, Latinen *et al*[14] were first to record the ultraviolet spectra of these monomers in liquid phase. Neither infrared nor Raman shifts are reported in literature. Only the infrared records are included in the Sadtler Standard Spectra Collections[15] in the region 2-15μ. The authors have first attempted to photograph the electronic spectra in the vapour phase and to record the intrared spectra in region 2.5-40μ.

Experimental

Hilger medium quartz spectrograph was employed to photograph the electronic spectra. Absorption columns of varying lengths—20 to 150 cm—having a side arm and tap to permit evacuation and filling the sample, the end flanges of which were sealed with quartz polished window-discs, were used. The absorbing vapours were heated up from room temperature (22°) to 100°C electrically. The optimum conditions of absorption at a certain pathlength were adjusted by just filling the sample gradually in steps and/or warming the cell. The cells were pre-evacuated to increase the absorbing vapour since dichlorostyrenes have very low vapour pressure at room tempeautre. Jets of dry and hot air were required to blow for preventing condensation of vapours on window-discs.

A Hilger hydrogen arc lamp served the purpose of continuous radiation and the atomic lines of iron for comparison. Exposures of 30 to 50 min. were required to photograph the absorption bands on Ilford N-40 plates

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with slit width of 30μ. The positions of the bands were measured on a Hilger comparator having a least count of 0.001 mm. and are ascertained upto ± 5 cm^{-1} for sharp and ± 10 cm^{-1} for diffuse and broad bands. Some of the bands were measured with pin-point marking in view of their weak intensity and diffuseness. They may be uncertain upto ± 15 cm^{-1} or more.

The infrared spectra in liquid capillary thicknesses were recorded with a Perkin Elmer 521 double beam spectrophotometer. The instrument setting was chosen for optimal spectral quality (total scan time 25 min., inverse dispersion 5 cm^{-1}/mm, automatic gain control and speed suppression). The positions of the bands are correct upto ± 1 cm^{-1}.

The pure monomers were obtained from Messrs. Koch-Light Laboratory of U.K. and were used as such.

Results

The molecules 2,5-DCS and 3,4-DCS absorb disceretely in the regions $\lambda\lambda$ (3100-2950) and $\lambda\lambda$ (3040-2890) respectively and about 45 bands, shaded to red, have been measured in each case. The molecules 2,6-DCS exhibits only a weak continuum centered at λ ($\sim$3050). The pure electronic transition, the 0,0 band in 2,5-DCS has been assigned at λ (3082.6), which appears strongly and is persistent at measure cases. In the case of 3,4-DCS, the 0,0 band appears at λ (3013.4). The excited state vibrational frequencies are observed to have values 137, 296, 454, 669, 999, 1104, 1217, 1319 and 1406 cm^{-1} in 2,5-DCS and 116, 261, 418, 605, 853, 991, 1098, 1217 and 1315 cm^{-1} in 3,4-DCS. As the band system does not extend much towards the longer wave length side from the 0,0 band in each of the spectrum, none of the ground state frequencies have been deciphered. The band satellites having the separation 32 and 60 cm^{-1} towards red and 21 and 63 cm^{-1} towards violet side of the 0,0 band have been interpreted as v-v transitions in 2, 5-DCS, while the frequency differences are 30, 52 and 75 cm^{-1} towards red and 40 cm^{-1} towards violet side in 3, 4-DCS. The remaining bands in each case have been assigned as summations of the excited state frequencies. Tables 1 and 2 present the details of the assignments of the ultraviolet absorption bands of 2,5-DCS and 3,4-DCS, respectively.

The number of absorption peaks read out from the infrared absorption curves are 43 in 2,5-DCS; 58 in 2,6-DCS and 57 in 3,4-DCS. Most of the intense absorptions have been observed as the fundamentals and the remaining as the summations/overtones in each case (Table 3). A correlation of the observed excited state frequencies and the infrared fundamental vibrations has been presented in Table 4, and their probable mode of vibrations have also been mentioned therein.

Discussion

Styrene molecule has the molecular plane as the only essential symmetry and belongs to C_s point group. A deviation from the coplanarity has been evidenced in the case of mono-substituted styrenes[12] due to the interaction between the vinyl and other basic groups. The possibility of further addition into this interaction is not improbable in the case of dichlorostyrenes. However, this interaction and thereby the deviation from the coplanarity may be ignored here to a first approximation for the understanding of the qualitative feature of the spectra, and dichlorostyrenes may also be assumed to belong to C_s point group as other substituted styrenes. Consequently, total 42 normal vibrations (30 of benzenoid origin plus 12 internal vibrations of vinyl group) consist of 29a′, symmetric and 13a″, asymmetric to the plane of the molecule. Vibrations of either of the species are allowed in electronic and vibrational spectra, and the intensity will largely depend upon the mode of benzene or ethylene from which these have been derived. Moreover, a general enhancement in intensity is a must in the vibrational spectra due to the conjugation of the vinyl groups in styrene and its derivatives[16].

In styrene, the longest wave length electronic transition is essentially due to the excitation of the π-electrons of the benzene ring[17], and shown to an analogue of benzene transition, $B_{2u} \leftarrow A_{1g}$, which in C_s symmetry transforms to an allowed transition, $A' \leftarrow A'$ in styrene and its derivatives.

As a consequence of the allowed nature of transition, the 0,0 band is located at 32431 cm^{-1} in 2,5-DCS and at 33175 cm^{-1} in 3,4-DCS, which appears most intense in the first group of the bands towards the longer wave length side of the each spectrum. The principal absorption bands towards the shorter wave length side of the 0,0 band have been interpreted due to the excitation of fundamental vibrations in the upper state. The choice of the assignment of the fundamental vibrations were their intensity and the combinability. Since the spectrum appears weak superimposed by a continuum (probably the second electronic transition), no definite conclusion about the progressions of various symmetric vibrations can be had from the inspection of the spectrogrammes, and thus the choice of the fundamentals in the electronic spectrum lies on to a tentative basis.

While discussing the actual mode of different observed fundamentals in the ultraviolet and infrared spectra, let us start with the identification of carbon vibrations of the

TABLE 1—ASSIGNMENTS OF THE ULTRAVIOLET ABSORPTION BANDS OF 2,5-DICHLOROSTYRENE VAPOUR

(All values are in cm^{-1})

ν_{vac}.	Separation form the 0,0 band	Assignments
32173 (ew)	−258	—
32209 (w)	−222	—
32246 (w)	−185	0−185 (?)
32277 (w)	−154	0−2×60−32
32307 (mw)	−124	0−2×60
32336 (ms)	−95	0−60−32
32371 (s)	−60	0−60
32399 (ms)	−32	0−32
32431 (s)	0	0, 0 band
32452 (mw)	21	0+21
32494 (ms)	63	0+63
32525 (w)	94	0+63+21
32549 (mw)	118	0+2×63
32568 (mw)	137	0+137
32599 (w)	168	0+296−2×60
32630 (mw)	199	0+296−60−32
32662 (w)	231	0+296−60
32698 (w)	267	0+296−32
32727 (mw)	296	0+296
32785 (w)	354	0+296+63, 0+454−60−32
32827 (ew)	396	0+454−60
32852 (ew)	421	0+454−32
32885 (mw)	454	0+454
32976 (ew)	545	0+669−2×60
33007 (ew)	576	0+669−60−32
33035 (w)	604	0+669−60, 0+2×296
33065 (ew)	634	0+669−32
33100 (mw)	669	0+669
33184 (w)	753	0+454+296
33230 (w)	799	—
33300 (w)	869	0+669+296−60−32
33336 (w)	905	0+669+296−60, 0+2×454, 0+999−60−32
33361 (ew)	930	0+669+296−32, 0+999−60
33388 (w)	957	0+669+296, 0+999−32
33430 (mw)	999	0+999
33483 (ew)	1052	0+999+63
33535 (mw)	1104	0+1104, 0+1217−2×60
33580 (w)	1149	0+1217−60
33648 (mw)	1217	0+1217
33700 (w)	1269	0+1217+63
33750 (mw)	1319	0+1319
33802 (w)	1371	0+1319+63
33837 (mw)	1406	0+1406

Letters in parentheses indicate the visual estimates of relative intensity as s = strong, m = medium, w = weak and e = extremely.

TABLE 2—ASSIGNMENTS OF THE ULTRAVIOLET ABSORPTION BANDS OF 3,4-DICHLOROSTYRENE VAPOUR

(All values are in cm^{-1})

ν_{vac}.	Separation from the 0,0 band	Assignments
32878 (ew)	−393	—
32915 (w)	−260	—
32941 (ew)	−234	0−2×75−52−30
32976 (w)	−199	0−2×75−52
33009 (w)	−164	0−2×75
33043 (mw)	−132	0−75−52
33063 (mw)	−112	0−75−30
33100 (ms)	−75	0−75
33123 (ms)	−52	0−52
33145 (ms)	−30	0−30
33175 (s)	0	0,0 band
33215 (mw)	40	0+40
33255 (w)	80	0+2×40
33291 (ms)	116	0+116 (?)
33329 (ew)	154	—
33369 (ew)	194	0+261−75
33436 (mw)	261	0+261
33478 (ew)	303	0+261+40
33501 (w)	326	—
33593 (mw)	418	0+418
33635 (ew)	460	0+418+40
33710 (w)	535	0+2×261
33744 (w)	569	0+2×261+40
33780 (ms)	605	0+605
33822 (mw)	645	0+605+40
33852 (mw)	675	0+418+261
33892 (w)	717	0+418+261+40
33940 (w)	765	0+853−52
33991 (w)	816	0+853−30
34007 (w)	832	0+2×418
34028 (ms)	853	0+853
34058 (w)	883	0+853+40, 0+261+605
34099 (ew)	924	0+853+2×40, 0+991−75
34130 (w)	955	0+991−30
34166 (ms)	991	0+991
34194 (mw)	1019	0+605+418
34201 (mw)	1029	0+991+40
34238 (w)	1063	0+991+2×40
34273 (ms)	1098	0+1098
34301 (mw)	1126	0+261+853
34308 (mw)	1133	0+1098+40
34354 (mw)	1179	0+1098+2×40
34392 (ms)	1217	0+1217
34425 (ew)	1250	0+1217+40, 0+261+991
34469 (ew)	1294	0+1217+2×40, 0+261+991+40
34590 (w)	1315	0+1315

TABLE 3—VIBRATIONAL ASSIGNMENTS OF INFRARED ABSORPTION BANDS OF LIQUID DICHLOROSTYRENES MONOMERS
(All values are in cm^{-1})

2,5-DCS	2,6-DCS	3,4-DCS	Assignments
—	330 (13)	315 (9)	β(C−Cl) symmetrical
—	345 (10)	326 (4)	β(C−Cl) asymmetrical
—	—	331 (2)	819−495
—	—	340 (3)	877−530
—	360 (9)	355 (2)	740−375, 716−367
—	375 (13)	367 (8)	ν_{18a}
—	—	376 (5)	687−315
—	—	387 (3)	716−326
418 (11)	400 (12)	410 (10)	ν_{20a}
—	—	415 (5)	819−410
428 (11)	415 (18)	430 (20)	δ(C−C = C) group
—	—	450 (7)	857−410
498 (43)	—	495 (15)	ν_{20b}
515 (7)	522 (12)	530 (5)	ν_{18b}
595 (31)	590 (9)	625 (18)	methylene wagging
630 (9)	630 (10)	630 (20)	C−Vinyl inplane deformation
—	640 (8)	638 (12)	983−345, 315+315
—	—	654 (3)	326+326
645 (18)	668 (6)	679 (27)	ν(C−Cl)
—	695 (10)	687 (40)	δ(C−C)
705 (2)	—	716 (15)	ν_2−ring breathing
740 (2)	—	—	1255−515
810 (90)	740 (83)	819 (53)	γ(C−H)
862 (56)	775 (96)	857 (53)	γ(C−H)
—	798 (83) sh	—	400+400 (?)
880 (68)	892 (16)	877 (40)	γ(C−H)
922 (77)	932 (82)	913 (45)	δ(= CH−) group
—	965 (35) sh	945 (2)	630+330, 630+315
985 (66)	983 (70)	981 (42)	δ(= CH_2) group
—	—	1023 (40)	ν_6—triagonal breathing
1045 (92)	1032 (39)	1027 (40)	β(C−H)
—	—	1038 (16)	530+495
1098 (94)	1090 (85)	1127 (55)	β(C−H)
1130 (47)	1148 (42)	1136 (32)	β(C−H)
—	1185 (67)	—	β(C−H)
1195 (37)	1210 (39)	1198 (25)	C−Vinyl stretching
—	—	1229 (4) sh	913+315
—	1240 (2) sh	1240 (2)	892+345, 913+326
—	—	1249 (15)	625+625
1250 (40)	1258 (40)	1256 (13)	methine rocking
1268 (22)	1270 (22) sh	1268 (35)	−, 932+330, 630+630
—	1300 (19)	1298 (5)	775+522, 981+315
1360 (19)	1350 (18)	1368 (35)	ν(C−C)
1395 (80)	1400 (78)	1383 (37)	ν(C−C)
1415 (74)	1430 (78)	1412 (8)	methylene scissoring
1455 (94)	1442 (87)	1467 (60)	ν(C−C)
1465 (89) sh	1460 (32) sh	—	1045+418, 740+522, 892+400
—	1485 (26)	—	740+740
—	1535 (38) sh	—	—
1550 (35)	1552 (78)	1550 (26)	ν(C−C)
1570 (23) sh	1560 (36) sh	—	1045+510, 1210+345
1580 (38)	1578 (57)	1580 (50)	ν(C−C)
1612 (16) sh	1612 (23)sh	—	810+810, 1032+590
1620 (40)	1628 (53)	1623 (12)	ν(C = C) group
1678 (6)	1660 (22)	1684 (6)	1255+418, 1258+400, 1368+315

TABLE 3—(*Contd*)—VIBRATIONAL ASSIGNMENTS OF INFRARED ABSORPTION BANDS OF LIQUID DICHLOROSTYRENES MONOMERS
(All values are in cm^{-1})

2,5-DCS	2,6-DCS	3,4-DCS	Assignments
1698 (8)	—	1698 (4)	1195+498, 1383+315
—	1710 (21)	1716 (1)	932+775, 1027+687
1745 (9)	1760 (22)	1740 (5)	1255+598, 1430+330, 1412+326
—	1788 (21)	—	1445+345
1835 (12)	1855 (31)	1825 (5)	1415+418, 922+922, 1442+415, 913+913
1860 (11)	1910 (21)	1885 (3)	1360+498, 1578+330, 1467+315
1872 (13)	1920 (21)	—	1455+418, 932+983
—	2000 (17)	—	1578+430
2835 (31)	2910 (32)	—	1415+1415, 1578+1430
2890 (36)	2965 (36)	2960 (2)	—, —, 1383+1580
—	2985 (37)	2978 (4)	methylene stretching
3010 (31)	3012 (38)	3000 (3)	methine stretching
3052 (37)	3045 (42)	3050 (4)	ν(C—H) aromatic
3080 (42)	3085 (42)	3075 (4)	asym. methylene stretching
—	3108 (35)	—	1552+1552
—	3145 (36)	—	1578+1578
—	3178 (31)	—	1552+1628
3575 (21)	3580 (36)	—	—

Figures in parentheses indicate per cent absorption. The following abbreviations are used to denote the mode of vibrations, ν= stretching, β= planar deformation, γ and δ= nonplanar deformations and sh = shoulder bands.

TABLE 4—CORRELATIONS OF THE EXCITED STATE AND THE INFRARED FREQUENCIES OF DICHLOROSTYRENES
(All values are in cm^{-1})

2,5-DCS		2,6-DCS	3,4-DCS		Assignments
I.R.	E.S.	I.R.	I.R.	E.S.	
—	137	—	—	116	γ(C—Cl)
—	296	375	367	261	ν_{18a}
515	454	522	530	418	ν_{18b}
645	—	668	679	605	ν(C—Cl)
705	669	—	716	—	ν_2—ring breathing
—	—	—	1023	853	ν_6—triagonal breathing
1045	999	1032	1027	991	β(C—H)
1130	1104	1148	1136	1098	β(C—H)
1195	1217	1195	1198	1217	(C—Vinyl) stretching
1395	1319	1400	1383	1315	ν(C—C)
1620	1406	1628	1623	—	ν(C = C) group

I.R. = Infrared, E.S. = Excited state.

benzene ring. There are essentially 8 carbon vibrations: $\nu_2(995)a_{1g}$ and $\nu_6(1010)b_{1u}$ ring breathings; $\nu_9(1309)b_{2u}$, $\nu_{13}(1482)e_{1g}$ and $\nu_{16}(1599)e_{2g}$ carbon stretchings; $\nu_{18}(608)e_{2g}$ planer ring deformation and $\nu_8(703)b_{2g}$ and $\nu_{20}(399)e_{2u}$ nonplanar ring deformations (the nomenclature of the modes are due to Herzberg[18]). In the electronic spectra of benzene and its derivatives much emphasis has been given in the identification of the ring breathings (ν_2 and ν_6 modes) and planar ring deformation, (ν_{18}). The occurrence of ν_{18} mode in substituted benzenes is often regarded as the system belonging to benzenoid origin. This mode splits into two component vibrations, designated as ν_{18a} and ν_{18b}, and in C_s symmetry, the lower one ν_{18a} becomes X-sensitive mode (the magnitude and the intensity of which are largely affected by the mass as well as the disposition of the substituent atoms or

substituent groups). The ν_{18b} mode depends upon the dispositions only. In the present case, the pairs of medium intense bands at 32727 and 32885 cm^{-1} in 2,5-DCS and at 33436 and 33593 cm^{-1} in 3,4-DCS have been classified due to the excitation of the excited state frequencies, 296 and 454 cm^{-1} in the former and 261 and 418 cm^{-1} in the latter case. The overtones of these frequencies have also been observed at 33035 and 33336 cm^{-1} in 2,5-DCS and at 33710 and 34007 cm^{-1} in 3,4-DCS with weak intensity. Moreover, an alternative explanation for these bands (overtones) has also been suggested (Tables 1 and 2). On the ground that these excited state frequencies seem to be of symmetrical nature, the frequencies 296 and 454 cm^{-1} in 2,5-DCS and 261 and 418 cm^{-1} in 3,4-DCS constitute the planar ring deformations and may be correlated with infrared fundamentals 515 cm^{-1} in the former (only ν_{18b} mode is observed) and 367 and 530 cm^{-1} in the latter molecule. While in the case of 2,6-DCS, the ν_{18a} mode is identified to have a value 375 cm^{-1} and the ν_{18b} mode 522 cm^{-1} in the infrared spectra. The magnitude and the intensity of the infrared fundamentals (ground state) corresponding to ν_{18} ring deformation have the comparable value in all the three isomers, but in the excited state the ν_{18b} mode has 12 per cent depression in going from 2,5 to 3,4-disposition.

In the assignment of ν_2 and ν_6 modes in the size of the molecules considered, the concept of the interaction of these two modes as developed in the case of disubstituted benzenes[19–21] is not only involved. Interactions among several symmetry as well as magnitude appropriate vibrations come into picture and the modes no longer remain isolated, but mixed together in asymmertically trisubstituted benzenes. Little work in this direction is available in literature and it is difficult to draw a definite conclusion about the way in which the borrowing is achieved. It is believed that the either of the ν_2 and ν_6 modes loses or gains the prominency in the molecules of the size considered at the expense of the C-X vibrations and C-Hydrogen deformations and *vice versa*. In the electronic spectrum of 2,5-DCS two excited state frequencies (669 and 999 cm^{-1}) and in 3,4-DCS, three excited state frequencies (605, 853 and 991 cm^{-1}) have been observed in the frequency range 600-1000 cm^{-1}. There is a little doubt to assign 999 cm^{-1} fundamental in 2,5-DCS and 991 cm^{-1} in 3,4-DCS to a C-Hydrogen planar deformation of the ring (having some ν_6-trigonal breathing character), and may be correlated with infrared frequencies 1045 and 1027 cm^{-1} in the respective molecules. The 669 cm^{-1} vibration in 2,5-DCS and 605 cm^{-1} in 3,4-DCS may belong to C-Cl stretching or ν_2-ring breathing. In the case of 2,5-DCS, the chlorine-atoms form para-axis and in the case of 3,4-DCS, the chlorine-atom at position 4 forms para-axis with vinyl group; the symmetrical C-Cl stretching in 2,5-DCS interacts in phase with ν_2-ring breathing and ν_2 level is pushed apart to C-Cl level, which is lower than ν_2 level. During this interaction C-Cl may lose its prominence, and the ν_2-ring breathing have some enhanced value and intensity as compared to those in 3,4-DCS. Consequently, 669 cm^{-1} vibration of 2,5-DCS assigned as the ν_2-ring breathing and 605 cm^{-1} vibration of 3,4-DCS to C-Cl stretching. These frequencies have been identified to have infrared values 705 and 679 cm^{-1}, respectively. And, indeed, the ring breathing 716 cm^{-1} (infrared value) of 3,4-DCS is less intense than the C-Cl stretching 679 cm^{-1} (infrared value), where in the case of 2,5-DCS, the ring breathing 705 cm^{-1} (infrared value) and C-Cl stretching 645 cm^{-1} (infrared value) have the comparable intensity. Further, this is also supported by the fact that the trigonal breathing is not observed in electronic and vibrational spectra of 2,5-DCS, the whole of the intensity may be borrowed to C-Hydrogen planar deformation 999 cm^{-1} (1045 cm^{-1} very intense infrared absorption). The third excited state frequency 853 cm^{-1} of 3,4-DCS is only assigned to triagonal breathing and is correlated to 1023 cm^{-1} medium intense infrared band, the intensity of which is also comparable to 1027 cm^{-1}, a C-Hydrogen planar deformation. These observations are also in accordance with those observed in some other similar trisubstituted benzenes e.g. the excited state frequencies are observed to have values 688 and 1011 cm^{-1} in 3,6-flouro-bromotoluene and 607 and 860 cm^{-1} in 4,3-fluorobromotoluene (Authors' unpublished work). In the case of 2,6-DCS the C-Cl stretching is weakly observed in the infrared spectra at 668 cm^{-1}. The ν_2 and ν_6 breathings have not been identified with fair certainty.

Each of the degenerate skelton carbon stretchings, ν_{13} and ν_{16} splits into two distinct vibrations in lower symmetry and their identification is straightforward. These have been observed at 1395, 1455, 1550 and 1580 cm^{-1} in 2,5-DCS; at 1383(?), 1467, 1550 and 1580 cm^{-1} in 3,4-DCS and at 1400, 1442, 1552 and 1578 cm^{-1} in 2,6-DCS. The excited state frequency 1319 cm^{-1} in 2,5-DCS and 1315(?) cm^{-1} in 3,4-DCS may be correlated to the lower component of the skelton stretching ν_{13} (1482)e_{1u}. The ν_9 (1309)b_{2u} carbon vibration is observed to have infrared value 1360 cm^{-1} in 2,5-DCS, 1368 cm^{-1} in 3,4-DCS and 1350 cm^{-1} in 2,6-DCS.

One of the non-planar ring deformations ν_{20} (399)e_{2u} is degenerate and splits into two component vibrations. In C_s symmetry the lower component ν_{20a} remains around 400 cm^{-1}, while the higher ν_{20b} depends upon the

disposition of the substituent only. The former vibration has been identified at 418 cm^{-1} in 2,5-DCS, at 400 cm^{-1} in 2,6-DCS and at 410 cm^{-1} in 3,4-DCS, while the latter mode is observed at 498 cm^{-1} (2,5-DCS) and 495 cm^{-1} (3,4-DCS). The non-degenerate $\nu_8(703)b_{2g}$ carbon deformation has been observed at 695 cm^{-1} in 2,6-DCS and at 679 cm^{-1} in 3,4-DCS. This vibration is not observed 2,5-DCS.

The hydrogen vibrations of benzene ring consist of $\nu_1(3073)a_{1g}$, $\nu_5(3057)b_{1u}$, $\nu_{12}(3064)e_{1u}$ and $\nu_{15}(3056)e_{1u}$ stretchings; $\nu_3(1350)a_{2g}$, $\nu_{10}(1146)b_{2u}$, $\nu_{14}(1037)e_{1u}$ and $\nu_{17}(1178)e_{2g}$ planar deformations and $\nu_4(674)a_{2u}$, $\nu_7(990)b_{2g}$, $\nu_{11}(846)e_{1g}$ and $\nu_{19}(967)e_{2u}$ nonplanar deformations. Two of each of the above sets of vibrations are degenerate and split into two distinct vibrations in lower symmetry. In C_s symmetry, the stretching and planar deformations transform to a′ and nonplanar to a″ vibrational species. Further, on substitution one of the stretching, planar and nonplanar deformations (for every substitution) become X-sensitive mode. In the case of trisubstituted benzenes (dichlorostyrenes), three of the stretchings and deformations become X-sensitive, C-X stretching and deformations (X stands for substitutent atom or group, here Cl-atom or vinyl group). Out of the two C-Cl stretchings (symmetrical as well as asymmetrical) only one has been observed in the electronic spectrum of 3,4-DCS (vide supra), while in the infrared spectra one vibration in each of 2,5-DCS (645 cm^{-1}), 2,6-DCS (668 cm^{-1}) and 3,4-DCS (679 cm^{-1}) has been identified. The excited state frequencies 137 cm^{-1} in 2,5-DCS and 116 cm^{-1} in 3,4-DCS may be assigned to nonplanar C-Cl deformations. The planar C-Cl deformations are observed at 330 and 345 cm^{-1} in 2,6-DCS and 315 and 326 cm^{-1} in 3,4-DCS in the infrared spectra only.

The C-vinyl stretching is invariably observed around 1200 cm^{-1} in the electronic and infrared spectra of styrene and its derivatives, and the magnitude does not change appreciably even in the excited state. In the present case, the excited state frequency 1217 cm^{-1} in each of 2,5-DCS and 3,4-DCS is assigned to this mode and may be correlated to infrared data 1195 cm^{-1} in 2,5-DCS and 1198 cm^{-1} in 3,4-DCS. While in the case of 2,6-DCS, the infrared frequency 1185 cm^{-1} has been assigned to C-vinyl stretching. Some increase in the magnitude of the excited state frequency as compared to ground state (infrared value) frequency has been observed in the case of mono-substituted styrenes, and this suggests that the C-vinyl bond goes under a little constrain in the excited state. The planar and non-planar deformations of C-vinyl group have not been observed with certainty, however, a weak band in the infrared spectra, which is also observed invariably around 630 cm^{-1} in the present case and also in mono-substituted styrenes (but not assigned previously) may be suggested to C-vinyl planar deformation.

One of the three hydrogen planar deformations of the ring has already been discussed in the case of 2,5-DCS and 3,4-DCS. One more excited state frequency in each of 2,5-DCS (1104 cm^{-1}) and 3,4-DCS (1098 cm^{-1}) has been assigned to this mode, observed at 33535 and 34273 cm^{-1} in the electronic spectra of these isomers. These frequencies may be correlated to infrared frequencies 1130 cm^{-1} in 2,5-DCS and 1136 cm^{-1} in 3,4-DCS. The remaining one planar hydrogen deformation in each of 2,5-DCS and 3,4-DCS has been identified at 1098 and 1127 cm^{-1} respectively, in the infrared spectra. The three such vibrations in 2,6-DCS are observed at 1032, 1090 and 1148 cm^{-1} in the infrared spectra. The nonplanar hydrogen deformation of ring lie in the region 700-950 cm^{-1} (Ref. 16). These frequencies have been observed to have values 810, 862 and 880 cm^{-1} in 2,5-DCS; 740, 775 and 892 cm^{-1} in 2,6-DCS and 819, 857 and 877 cm^{-1} in 3,4-DCS.

The C = C stretching and the C-Hydrogen deformations constitute the internal vibrations (so called characteristic group frequency) of the vinyl group, which are derived from the ethylenic modes. A distinct sharp and strong singlet infrared absorption around 1630 cm^{-1} is caused by the vinyl C = C stretching in styrene and its derivatives. This frequency is also observed in the electronic spectra, but the magnitude of the excited state value is markedly lowered down to 1400 cm^{-1}. This depression is accounted by the lesser conjugation of the vinyl group with phenyl ring in the excited state. It is believed that in the excited state, the molecules (styrene and its derivatives), no longer remained of planar configuration (deviation from coplanarity in excited state) and the C = C bond resets to a increased value (lengthening in the bond), while C-vinyl bond goes to a little constrain. It is why the C-vinyl stretching in the excited state is of somewhat higher value as compared to ground state value. However, this constrain is negligible to the lengthening in C = C bond. The excited state C = C stretching in the electronic spectra has been assigned to 1406 cm^{-1} fundamental in the case of 2,5-DCS, while no such vibration has been observed in 3,4-DCS. The infrared fundamentals corresponding to this mode occur at 1620 cm^{-1} in 2,5-DCS; 1628 cm^{-1} in 2,6-DCS and 1623 cm^{-1} in 3,4-DCS.

There are three possible vibrations of C-H bonds: asymmetric and symmetric stretchings of the internal methylene (= CH_2), and a stretching of internal methine (—CH =). Literature references[16,23–24] give the normal

positions at 3085$\pm$10 cm^{-1} for asymmetric mode, 2980$\pm$15 cm^{-1} for symmetric mode and 3025$\pm$ cm^{-1} for the methine mode. In the case of vinyl aromatics, the C-H stretching of the ring may interfere with the symmetric as well as asymmetric stretchings of the terminal methylene and the alkyl C-H stretching to the stretching of internal methine. However, a close examination of the infrared spectra of similar molecules, having different basic group may enable to locate the different C-H stretchings. In styrene and its derivatives, the asymmetric band at 3080 cm^{-1} predominates. The other two bands are noted at 3020$\pm$10 cm^{-1} and 2985$\pm$10 cm^{-1} as shoulders on the side of the aromatic and aliphatic C-H stretchings. In the present case these stretchings are identified at 3010 and 3080 cm^{-1} in 2,6-DCS and at 2978, 3000 and 3075 cm^{-1} in 3,4-DCS. The remaining one frequency in this region in each molecule (3052 cm^{-1} in 2,5-DCS, 3045 cm^{-1} in 2,6-DCS and 3050 cm^{-1} in 3,4-DCS) is safely assigned to aromatic C-H stretching.

Further, there are three possible deformations of the vinyl group within its own plane, a scissoring motion and a rocking motion of the terminal methylene, and a rocking motion of the terminal methine. The scissoring mode normally is seen an intense band and it has an over-all range of 1400-1430 cm^{-1}. This mode is located at 1415 cm^{-1} in 2,5-DCS; 1430 cm^{-1} in 2,6-DCS and at 1412 cm^{-1} (weak ?) in 3,4-DCS. The band caused by the rocking deformation of the internal methine is identified at 1255 cm^{-1} in 2,5-DCS, 1258 cm^{-1} in 2,6-DCS and 1256 cm^{-1} in 3,4-DCS. The third deformation band, due to the rocking of the thermal methylene, is usually a shoulder or a weak band located around 1090 cm^{-1} (Ref. 23). In the present case, this mode is not observed in any one of the molecules. This might have been superimposed by strong C-H deformation of the ring, which occurs around the same region.

Since there is no element of symmetry within the vinyl group except for the plane of the five atoms making up the group, there should be three different infrared active nonplanar deformations of the C-Hydrogens. The first of these is always observed strongly around 990 cm^{-1} in styrene and its derivatives, and caused by a deformation that is essentially a twisting about the double bond. The second of these bands (strong absorption) is found near 910 cm^{-1}, and is caused by a wagging motion of the terminal methylene. The third mode may be closely related in both intensity and location to the planar deformation of the C-vinyl group around 600 cm^{-1} (?). These modes are located at 922, 985 and 595 cm^{-1} in 2,5-DCS; 932, 985 and 590 cm^{-1} in 2,6-DCS and 913, 981 and 625 (?) cm^{-1} in 3,4-DCS. The first overtones and summations of twisting and wagging modes are also significant.

Electronic Behaviour: To the fact that the molecules 2,5-DCS and 3,4-DCS exhibit weak discrete absorption, and the molecule 2,6-DCS does not, may be accounted due to the steric/ortho-interaction followed by the usual inductive and mesomeric interactions between the adjacent chlorine-atoms and the vinyl group. The molecular state of isomer 3,4- may be supposed to be free from the ortho-interaction between the chlorine-atoms and the vinyl group (although two adjacent chlorine-atoms at positioned 3 and 4 may interact together), and the molecule exhibits best discreteness in all the three dichlorostyrenes studies. In the case of 2,5-DCS, only one chlorine-atom is adjacent to the vinyl group and affect the molecular state moderately and the vibronic discreteness is lost somewhat as compared to 3,4-DCS. But, in 2,6-DCS, there are two adjacent chlorine-atoms to the vinyl group, and their interactions affect markedly the molecular state, and it is why discreteness is observed not at all. On these grounds, among all the six isomers of dichlorostyrenes the isomer 3,5-DCS may exhibit the best discreteness, while 2,3- and 2,4-DCS may have feature like that in 3,4-DCS. Moreover, no semi-quantitative empirical prediction can be made at this moment.

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Studies have been carried out during 1968-69 and 1969-70 to determine the effect of varying levels of nitrogen application and the relative efficacy of soil and half soil + half foliar (1 per cent) applications of urea on yield of Pusa Purple Long (PPL) and Pusa Purple Cluster (PPC) varieties of brinjal. The results showed that increase in yield was obtained with the increasing levels of nitrogen in both the varieties but no significant difference was found with respect to the method of application. The yield of the PPL variety was significantly higher than that of PPC. In both the varieties, the highest yield through soil application was obtained at 80 kg nitrogen/ha except in PPL at 120 kg nitrogen/ha in one season. The highest yield by half soil and half foliar application in both the varieties was found at 40 kg nitrogen/ha, except in PPC which produced a higher yield at 80 kg nitrogen/ha in one season. In both the varieties, application of 40 kg nitrogen/ha as half soil and half foliar was found as efficient as 80 and 120 kg nitrogen/ha, except in PPC in 1969-70. From the experimental data, the optimal dose (at cost price of Rs. 500.00/tonne of brinjal and Rs. 81.85/40 kg of urea nitrogen) works out at 105 and 69 kg nitrogen/ha for PPL and PPC respectively as soil application and 67 and 65 kg nitrogen/ha respectively as half soil and half foliar applications.

Studies on the Relative Efficiencies of Soil And Foliar Application of Urea on Brinjal (*Solanum Melongena* L.)

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In recent years, foliar application of urea has been used satisfactorily as a source of nitrogen for a number of crops. Bhaumik[1] reported the results of investigations carried out in India on different crops, like sugarcane, wheat, paddy, jute, tobacco, etc., and indicated that foliar application of urea increased the yield appreciably in all the crops. In vegetable crops also, viz. brinjal and radish, Mitra and De[2] and Ray and Seth[3] respectively

have found the efficacy of foliar application of fertilizers which resulted in more net income than the application through soil. Considering these, the present investigation was designed to study the relative efficacy of soil and spray application of urea and to determine the optimum level of nitrogen requirement for the two varieties of brinjal.

Materials and Method

The two varieties of brinjal, viz. Pusa Purple Long and Pusa Purple Cluster, were grown at four levels of nitrogen (0, 40, 80 and 120 kg/ha) with a uniform basal application of 50 kg/ha of P_2O_5 and K_2O as single superphosphate and muriate of potash respectively. Urea was used as nitrogenous fertilizer and was applied by two different methods. 50 per cent urea was applied as basal and the rest 50 per cent was applied in six split doses at an interval of 10 days either as spray or as top-dressing to soil commencing the first spray or top dressing 30 days after transplanting. The concentration of urea spray was 1 per cent.

The experiment was conducted on a soil of an average fertility having pH 7.9, conductivity 0.14, available P_2O_5 1.89 kg/ha and organic carbon (0.145 per cent).

The design of the experiment was split plot with 3 replications. Variety X levels of nitrogen were under main plot and the methods were under subplot. The total number of plots was 48 and the net plot size was 5.6×4.2 sq.m. Transplanting was done in August and harvesting was continued till January next in both the years. The rows were 70 cm. apart and the plants 70 cm. apart within the row. The harvesting of full-grown tender fruits before the colour fades was done in every week. The experiment was conducted during the autumn in 1968-69 and 1969-70.

Results

The yield data for 1968-69 and 1969-70, analysed separately, are presented in Tables 1 and 2 respectively.

The statistical analysis of the data of 1968-69 showed significant difference in the yield between the levels of application of nitrogen and between the varieties but not in the methods of application. The application of nitrogen in all the levels gave significantly higher yield than the control in the variety Pusa Purple Long, but in the variety Pusa Purple Cluster the significant difference was observed only upto 80 kg nitrogen/ha level. Control and 120 kg/ha of nitrogen application did not differ significantly in the case of Pusa Purple Cluster. Although an increasing trend in yield was obtained upto 80 kg/ha in PPL and 40 kg/ha in PPC, no significant difference was obtained amongst N_1, N_2 and N_3 levels in both the varieties.

TABLE 1—EFFECT OF SOIL AND FOLIAR APPLICATION OF UREA AT VARYING LEVELS OF YIELD ON BRINJAL DURING 1968-69, TE/HA.

	Soil	Foliar	Mean
	Variety: Pusa Purple Long (V_1)		
N_0	14.83	14.53	14.68
N_1	20.88	27.84	24.36
N_2	36.40	23.87	30.13
N_3	29.66	20.47	25.06
Mean	25.44	21.68	23.56
	Variety: Pusa Purple Cluster (V_2)		
N_0	6.97	8.66	7.81
N_1	17.78	24.97	21.12
N_2	18.40	17.43	17.91
N_3	10.65	12.26	11.45
Mean	13.45	15.70	14.57
G. Mean	19.44	18.69	19.06

1. C.D. at 5% level between two main treatments means = 8.40 te/ha
2. C.D. at 5% level between two sub-treatments means at the same level of main treatment = 4.37 te/ha
3. C.D. at 5% level between two main treatments means at the same level of sub-treatment or at different levels of sub-treatment = 10.43 te/ha
4. Standard error of difference between two sub-treatment means = +1.456 te/ha

In both the varieties, foliar application of nitrogen at 40 kg/ha level gave significantly higher yield over the soil application method. At the N_2 and N_3 levels, soil application, on the other hand, proved significantly better in PPL but not in PPC variety.

In the PPL variety, the highest yield, viz. 36.4 te/ha, was recorded at N_2 through soil application; the highest yield (27.8 te/ha) by foliar method was found at N level, but the difference between the yields of these two sub-treatments was not significant. In the PPC variety, the highest yield, viz. 24.4 te/ha, was obtained at N level through foliar method, but no significant difference was observed between this treatment and the treatment (N_2 level) producing the highest yield through soil application method.

The analysis of 1969-70 data also showed similar

TABLE 2—EFFECT OF SOIL AND FOLIAR APPLICATION OF UREA AT VARYING LEVELS ON YIELD OF BRINJAL DURING 1969-70, te/ha.

	Soil	Foliar	Mean
	Variety: Pusa Purple Long (V_1)		
N_0	15.83	16.46	16.14
N_1	23.4)	31.16	27.28
N_2	24.28	26.28	25.28
N_3	27.65	23.84	25.74
Mean	22.79	24.43	23.61
	Variety: Pusa Purple Cluster (V_2)		
N_0	5.70	8.49	7.09
N_1	13.49	13.34	13.41
N_2	15.78	14.30	15.04
N_3	13.03	13.26	13.14
Mean	12.00	12.35	12.17
G. Mean	17.39	18.39	17.89

1. C.D. at 5% level between two main treatments means = 5.17 te/ha
2. C.D. at 5% level between two sub-treatments means at the same level of main treatment = 5.83 te/ha
3. C. D. at 5% level between two main treatments means at the same level of sub-treatment or at different levels of sub-treatment = 6.60 te/ha
4. Sandard error of difference between two sub-treatments means = +2.06 te/ha

trends as those in previous year, viz. significance in the main treatments (level × variety) and non-significance in sub-treatments (methods of application).

Application of nitrogen in all the levels gave significantly higher yields than that of control in both the varieties but there was no significant difference amongst N_1, N_2 and N_3 levels of nitrogen application. In this year also when the two methods of fertilizer application are compared separately, it was found to be non-significant. However, like previous year foliar application proved to be significantly better only at 40 kg nitrogen level in the PPL variety, but unlike in the previous year in the variety PPC foliar feeding could not prove to be superior to soil application at any level of nitrogen application.

Optimal Dose: In order to find out the optimal dose of nitrogen for soil and foliar applications for both the varieties, a quadratic equation of the type, $Y = yo + bx + cx^2$, was fitted on the average value of yield obtained in both the years and the four equations, thus obtained, are given below.

For V_1 (S) $Y = 14.7 + 11.2x - 2.1x^2$

V_2 (S) $Y = 6.3 + 12.7x - 3.6x^2$

V_1 (F) $Y = 16.5 + 14.3x - 4.2x^2$

V_2 (F) $Y = 9.3 + 11.0x - 3.3x^2$

where Y = yield of brinjal, tes/ha, and

x = 40 kg. of nitrogen/ha as one unit.

The expected values of yield of brinjal (te/ha) at different levels of nitrogen application, as obtained from the above equations, as well as the values obtained from the experimental results averaged over two years are presented in Table 3.

The optimal dose of nitrogen obtained from the above equations (giving price of one tonne of brinjal @ Rs. 500/- and 40 kg nitrogen as urea as Rs. 81.85) worked out to 105 kg nitrogen/ha and 69.60 kg/ha for V_1 and V_2 respectively when applied through ½ soil and ½ foliar method of application the optimal doses were 67.2 kg/ha and 65.6 kg/ha for PPL and PPC respectively under same cost-price ratio.

Discussion

On a critical examination of the yields for two seasons, it was found that the two varieties of brinjal behaved differently at different levels of nitrogen application.

TABLE 3—EXPECTED AND OBSERVED VALUES OF BRINJAL YIELD, TE/HA

Level of Nitrogen	Soil				Foliar			
	V_1(PPL)		V_2(PPC)		V_1(PPL)		V_2(PPC)	
	Expected	Observed	Expected	Observed	Expected	Observed	Expected	Observed
N_0	14.7	15.3	6.3	6.3	16.5	15.5	9.3	8.6
N_1	23.8	22.1	15.4	15.6	26.6	29.5	17.0	18.9
N_2	28.7	30.3	17.3	17.1	28.3	25.1	18.1	15.9
N_3	29.4	28.6	12.0	11.8	21.6	22.1	12.6	12.8

Undoubtedly, the PPL variety was significantly superior to PPC so far the yield of brinjal was concerned. Hence, the requirement of nitrogen for PPL was fairly high (105 kg/ha) as compared to that of PPC (69 kg/ha) so far soil application was concerned.

In general, there was no significant difference between the two methods of fertilizer application. Half-soil + half foliar method, however, gave significantly higher yield as compared to that of soil application method in both the varieties at 40 kg nitrogen/ha level especially in the first year. But its effect was not pronounced at higher levels of nitrogen application which might be due to the adverse effect of larger quantities of nitrogen application through foliage. This indicated the limitation of foliar feeding.

It may be noted that in both the varieties excluding PPC in 1969-70, the foliar application of nitrogen at 40 kg level produced fairly high yields which are comparable with the yields at higher levels of nitrogen application through soil. This is definitely an advantage so far fertilizer economy is concerned. This finding was in corroboration with those of Mukherjee and De[3] on potato, Ray and Seth[4] on radish and Mitra and De[2] on brinjal. But as regards the dose, our findings are contrary to those of Mitra and De[2] who reported that application of 80 kg nitrogen/ha, half through soil and half through foliage, was as efficient as 120 kg nitrogen/ha application in full through soil. This difference was probably due to the differential behaviour of different varieties under different agroclimatic conditions.

In the case of PPC although an increased yield of 3.64 tes over control was obtained during 1968-69 at 120 kg nitrogen/ha level the difference was not found significant but in 1969-70, the difference was significant. In both the years, the yield at 120 kg nitrogen/ha level appreciably decreased in the said variety. This may be due to imbalance resulted by the application of excessive nitrogen beyond its requirement at fixed levels of phosphorus and potash. It may be mentioned here that the optimal dose of nitrogen for PPC seems to be 69.60 kg/ha when applied through half soil and half top dressing (soil) method. The behaviour of PPC to foliar feeding of nitrogen towards production of brinjal was different in two seasons, as a result the optimal dose of nitrogen requirement both for soil and $\frac{1}{2}$ soil + $\frac{1}{2}$ foliar application was almost equal. Hence, the optimal dose of nitrogen requirement as $\frac{1}{2}$ soil + $\frac{1}{2}$ foliar cannot be indicated from the present study.

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In an investigation on the pest infestation in brinjal, it was observed that the incidence of leaf hoppers and aphids was directly related to the levels of nitrogen application irrespective of forms of nitrogen applied and varieties of brinjal tested. The fruit borer infestation, however, was related mainly to the varietal characters of the host plant. The Ramnagar variety had the maximum borer infestation compared to the two other varieties, viz. Pusa Purple Long and Pusa Purple Cluster.

An yield increase of 69 per cent was obtained with the highest dose of nitrogen (120 kg N/ha) followed by 45 per cent with the next lower dose (60 kg N/ha) over the control plots.

The application of Phosphamidon reduced considerably the pest population in the host plants, thereby an increase of nearly 20 per cent of the fruit yield was obtained in the treated plots. No positive interaction between the insecticide and doses and forms of nitrogen was, however, observed in this investigation with the yield of brinjal.

Studies on the Influence of Different Doses of Nitrogenous Fertilizers on the Incidence of Pests in Several Varieties of Brinjal Plant

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Introduction

Brinjal is one of the most important vegetables grown throughout the country, particularly in the northern India. Its cultivation is often restricted by certain insect pests out of which leaf hoppers (*Empoasca spp.*), aphids (*Aphis gossypii* Glover), 'Hadda' beetles (*Epilachna spp.*) and fruit-borers (*Leucinodes orbonalis* Guen.) are most important. The insects, like leaf hoppers and aphids, not only suck the sap of the plants but also transmit virus diseases, like little leaf, mosaic, etc., while the fruit-borer lays eggs in the young fruits and destroys the crop. Jotwani and Swarup[1] while working in detail with the control schedule of brinjal crop against fruit-borer (*L. orbonalis* Guen.), pointed out that about 15 per cent of the crop was damaged by this pest in control plots having no insecticidal application. The leaf hopper population was also considerably increased in the control plots. Peswani and Lal[2] reported a loss of 20.7 per cent in the Pusa Purple Long variety when the entire infested fruit was considered unusable. The actual damaged portion inside the fruit constitutes 9.7 per cent of the total fruit yield. Several earlier workers also indicated the seriousness of the borer and other pests of brinjal.[3-5]

It has been observed by several workers that insect population can be affected by varying the constituents of essential plant nutrients available to the host plants. In some cases, plants normally resistant to a particular species of insects apparently have become susceptible when grown in a medium having a deficiency or an excess of a certain element. The high and unbalanced nitrogenous manuring was attributed among other things to be the secondary cause for the high intensity of *Pyrilla* attack in sugarcane fields[6]. Tanada and Holdway[7] reported that tomato plants grown at higher level of nitrogen attracted more adult tomato bugs than others. Similarly, the fecundity of the aphids (*Aphis craccivora* Koch) was noticed to be more on the plants grown in solution high in nitrogen content. The chemical analysis of the plant indicated that phosphorus or potassium had no influence on the fecundity of that species.[8] Kundu and Pant[9], however, could not get any significant difference in the fecundity and longevity of mustard aphid (*Lipaphis erysimi*) (Kalt.) with increased doses of nitrogen in the nutrient media.

Therefore, an experiment was undertaken to determine the incidence of these pests on several varieties of

brinjal under different levels and forms on nitrogen application in the soil.

Experimental

Materials and Method: The field was prepared and farmyard manure was applied uniformly @ ten cartloads/hectare. Three types of nitrogenous fertilizers, viz. urea, ammonium sulphate and ammonium sulphate nitrate, with three levels, i.e. 0, 60 and 120 kg per hectare, and three varieties, viz. Pusa Purple Long, Pusa Purple Cluster and Ramnagar, were taken under a $3 \times 3 \times 3$ partially confounded factorial design and under each treatment there were to sub-treatments, i.e. insecticide and no insecticide application. There were two replications.

25 days old brinjal seedlings were transplanted in plots of 12 sq. m. with plants and rows 80 cm. apart. Each plot was then divided into two equal sub-plots and one of the sub-plots in each plot was treated with 0.05 per cent concentration of Phosphamidon at 15 days' interval @ 500 l./ha.

The other recommended cultural practices were followed as usual. 40 kg. of each of phosphate and potash were applied in the forms of single superphosphate and muriate of potash respectively as a basal dose. The nitrogenous fertilizers were applied in two split doses, viz. half at the time of land preparation and the remaining during the earthing up operation.

Estimation of Population of External Pests (Aphids and Leaf Hoppers): Of the several pests infesting brinjal, only leaf hoppers and aphids appeared in appreciable numbers mostly in the early stages of the crop and therefore, observations of these pests at different ages of the plants were recorded for these two pests only. The population counts of leaf hoppers and aphids were taken by first selecting at random four plants from each sub-plot and examining carefully each plant during early hours in the morning when the pests were not very active. The counts were taken at four different ages of the plant.

Estimation of the Population of Fruit-Borer: At each picking, all fruits, big as well as small ones, were plucked and examined for fruit-borer infestation. Those showing exit holes could be easily separated whereas others were carefully examined for the indication of the entry points of larvae in the form of small holes surrounded by small decolorized patches. The affected fruits were weighed separately to get the percentage of the infested fruits.

Nitrogen Percentage of the Leaves: For determining the relation between the nutrient uptake of the plant and pest incidence, the nitrogen percentage of the leaves were determined. The leaves were collected from each plot separately just after 4 P.M. and allowed to dry in an oven. Then the leaves were ground and the nitrogen content of the leaves were determined by Micro-Kjeldahl method.

Yield: The fruits were harvested at definite interval from each plot separately and the weights were recorded. Ultimately, the weight of the total yield per plot was calculated after the last harvest. In this experiment ten numbers of plants were planted in each sub-plot. But subsequently, some of the plants died out due to reasons beyond our control. Therefore, covariance technique was adopted and the yield of the plots was adjusted by the following equation:

$$Yijk - {}_{B}w\,(Xij. - Xi.) - {}_{B}s\,(Xijk - Xij.),$$

where ${}_{B}w$ is the regression coefficient of Y on X for the whole plot and ${}_{B}s$ for the sub-plot.

Yijk is the yield at ith replication and jth whole plot treatment nimber and kth split plot treatment number.

Results and Discussion (Pest incidence)

Leaf Hopper: In order to find out the leaf hopper incidence at different ages of the plant the leaf hopper count was recorded at 15 days interval (Table 1).

The result indicated that at the first count the difference between zero level of nitrogen with that of first level (60 kg. N/ha) and second level (120 kg. N/ha) averaged over types and varieties were significant at 5 per cent level. The difference of leaf hopper incidence between first and second level of nitrogen was found to be significant at 5 per cent level. The leaf hopper infestation gradually increased with the increase in the level of nitrogen application.

In the subsequent observations, i.e. in the 2nd, 3rd and 4th, a similar trend in the increase in leaf hopper infestation was obtained with the increase in the dose of nitrogen application.

No significant difference was obtained in the leaf hopper population between the types of nitrogenous fertilizers applied in the soil. However, only in the 1st observation the leaf hopper infestation was the highest in ammonium sulphate and was significantly higher than urea and ammonium sulphate nitrate (Table 1). Interaction effects were found to be non-significant at 5 per cent level in all the obseıvations.

Aphid: The aphid population was also counted at 15 days' interval as in the case of recording leaf hopper infestation. The results (Table 2) indicated that the differences in the infestation between the zero, the first and the second level of nitrogen averaged over types and

TABLE 1—LEAF HOPPER INFESTATION AT DIFFERENT AGES OF BRINJAL PLANTS
(FIGURES ARE IN LOG SCALE)

1ST OBSERVATION (45 DAYS OLD PLANT)

Treatments / Varieties	Type of N Fertilizer			Level of N, kg/ha			Mean
	Urea	Ammonium Sulphate	Ammonium Sulphate Nitrate	0	60	120	
Pusa Purple Long	0.648	1.009	1.044	0.784	0.707	1.210	0.900
Pusa Purple Cluster	0.903	0.944	0.794	0.614	0.893	1.134	0.880
Ramnagar	0.787	1.251	1.067	0.641	1.230	1.234	1.035
Mean	0.779	1.068	0.968	0.680	0.943	1.193	0.938
N — 60	0.692	1.166	0.972	C.D. at 5% level for marginal means			= 0.193
N — 120	1.050	1.283	1.245	C.D. at 5% level for means			= 0.335
2nd observation (60 days old plant)							
Pusa Purple Long	0.873	0.916	1.068	0.622	0.964	1.271	0.952
Pusa Purple Cluster	0.940	0.986	0.921	0.639	0.957	1.251	0.949
Ramnagar	0.843	0.930	0.991	0.701	0.887	1.175	0.921
Mean	0.885	0.944	0.993	0.654	0.936	1.233	0.941
N — 60	0.934	0.931	0.944	C.D. at 5% level for marginal means			= 0.117
N — 120	1.211	1.203	1.284	C.D. at 5% level for means			= 0.203
3rd observation (75 days old plant)							
Pusa Purple Long	1.048	0.937	1.138	0.619	1.104	1.400	1.041
Pusa Purple Cluster	0.940	1.010	0.915	0.468	1.037	1.360	0.955
Ramnagar	0.955	0.997	0.898	0.526	0.883	1.440	0.950
Mean	0.981	0.981	0.984	0.538	1.008	1.400	0.982
N — 60	0.929	1.081	1.014	C.D. at 5% level for marginal means			= 0.204
N — 120	1.445	1.357	1.397	C.D. at 5% level for means			= 0.353
4th observation (90 days old plant)							
Pusa Purple Long	1.145	1.106	1.228	0.836	1.028	1.514	1.126
Pusa Purple Cluster	1.176	1.186	1.172	0.774	1.295	1.466	1.178
Ramnagar	0.902	1.171	1.130	0.782	0.969	1.452	1.068
Mean	1.074	1.154	1.143	0.797	1.098	1.477	1.124
N — 60	1.001	1.089	1.202	C.D. at 5% level for marginal means			= 0.153
N — 120	1.629	1.442	1.360	C.D. at 5% level for means			= 0.266

TABLE 2—APHID INFESTATION AT DIFFERENT AGES OF BRINJAL PLANTS (FIGURES ARE IN LOG SCALE)

1ST OBSERVATION (45 DAYS OLD PLANT)

Treatments / Varieties	Type of N Fertilizer: Urea	Ammonium Sulphate	Ammonium Sulphate Nitrate	Level of N, kg/ha: 0	60	120	Mean
Pusa Purple Long	1.578	1.364	2.119	1.407	1.635	2.019	1.687
Pusa Purple Cluster	1.709	1.825	1.755	1.444	1.656	2.189	1.763
Ramnagar	1.618	1.773	1.747	1.451	1.775	1.912	1.713
Mean	1.635	1.654	1.874	1.434	1.689	2.040	1.721
N — 60	1.795	1.492	1.780	C.D. at 5% level for marginal means			= 0.219
N — 120	2.023	1.917	2.185	C.D. at 5% level for means			= 0.379
2nd observation (60 days old plant)							
Pusa Purple Long	2.148	2.118	2.199	1.846	2.130	2.489	2.155
Pusa Purple Cluster	1.958	2.026	2.156	1.502	2.161	2.477	2.046
Ramnagar	2.084	2.042	2.112	1.626	2.136	2.476	2.079
Mean	2.063	2.062	2.156	1.658	2.142	2.481	2.093
N — 60	2.231	2.014	2.181	C.D. at 5% level for marginal means			= 0.129
N — 120	2.373	2.498	2.572	C.D. at 5% level for means			= 0.223
3rd observation (75 days old plant)							
Pusa Purple Long	2.110	2.067	2.144	1.842	2.186	2.293	2.107
Pusa Purple Cluster	1.988	2.018	1.924	1.548	2.111	2.271	1.977
Ramnagar	2.070	1.834	2.225	1.737	1.999	2.393	2.043
Mean	2.056	1.977	2.098	1.709	2.099	2.319	2.042
N — 60	2.196	1.900	2.200	C.D. at 5% level for marginal means			= 0.152
N — 120	2.313	2.291	2.353	C.D. at 5% level of means			= 0.263
4th observation (90 days old plant)							
Pusa Purple Long	2.094	2.315	2.221	1.723	2.045	2.529	2.210
Pusa Pruple Cluster	1.897	2.003	1.905	1.495	1.955	2.355	1.935
Ramnagar	1.823	1.914	1.695	1.432	1.709	2.291	1.811
Mean	1.938	2.077	1.940	1.550	2.014	2.392	1.985
N — 60	1.947	2.078	1.851	C.D. at 5% level for marginal means			= 0.264
N — 120	2.442	2.381	2.352	C.D. at 5% level for means			= 0.457

varieties were significant at 5 per cent level. The difference between the first and the second level of nitrogen was also found to be significant. The aphid infestation gradually increased with the increase in the doses of nitrogen. The same trend was obtained in all the four observations taken at different ages of the plant.

The interaction between variety and type was found to be significant and the maximum infestation was observed in the Pusa Purple Long variety with the highest nitrogen level of ammonium sulphate nitrate and the lowest with ammonium sulphate. But this was only observed in the first observation and was absent in subsequent observations.

Fruit Borer: The Ramnagar variety was observed to

TABLE 3—AVERAGE FRUIT-BORER INFESTATION IN DIFFERENT TREATMENTS (ANGULAR TRANSFORMED FIGURE)

(a) Main treatment means

Treatments / Varieties	Type of N Fertilizer: Urea	Ammonium Sulphate	Ammonium Sulphate Nitrate	Level of N, kg/ha: 0	60	120	Mean
Pusa Purple Long	19.89	23.00	20.55	25.61	17.64	20.20	21.15
Pusa Purple Cluster	24.40	21.25	20.67	22.25	23.62	20.45	22.11
Ramnagar	36.74	29.93	35.18	38.74	31.89	31.22	33.95
Mean	27.01	24.73	25.47	28.87	24.38	23.96	25.74
N — 60	23.19	23.98	25.98	C.D. at 5% level for the marginal means			= 6.06
N — 120	23.24	25.33	23.30	C.D. at 5% level for the means			= 10.50

(b) Sub-treatment means

Varieties / Insecticides	Pusa Purple Long	Pusa Purple Cluster	Ramanagar	Mean
Untreated	23.22	23.56	38.82	28.53
Treated with (0.05%) Phosphamidon	19.08	20.65	29.08	22.94

C.D. at 5% level for the sub-treatment marginal means 2.27
C.D. at 5% level for the two sub-treatment means at the same level of main treatments 3.93
C.D. at 5% level for two main treatments means at the same level of sub-treatments 7.53.

be more susceptible than the other two varieties under trial (Table 3). The borer infestation in this variety was significantly higher than the other two varieties. There was no significant difference in the infestation between the Pusa Purple Long and Pusa Purple Cluster varieties. No significant difference was obtained between the levels and types of nitrogen application so far the borer infestation was concerned. The plots treated with 0.05 per cent Phosphamidon had significantly lower borer infestation than those of the untreated plots.

Nitrogen Percentage of Different Varieties of Brinjal under Levels and Types of Fertilizer Application: The analysis for nitrogen in leaves (Table 4) showed that with the increase in level of nitrogen application there was a

TABLE 4—MEAN PERCENTAGE OF NITROGEN OF THE LEAVES OF BRINJAL PLANTS

Treatments / Varieties	Type of N Fertilizer: Urea	Ammonium Sulphate	Ammonium Sulphate Nitrate	Level of N, kg/ha: 0	60	120	Mean
Pusa Purple Long	2.85	2.81	2.39	2.38	2.72	2.95	2.69
Pusa Purple Cluster	2.84	2.65	2.84	2.43	2.72	3.19	2.78
Ramnagar	2.92	2.90	2.55	2.52	2.56	3.29	2.79
Mean	2.87	2.79	2.60	2.44	2.67	3.14	2.75
N — 60	2.84	2.82	2.34	C.D. at 5% level for the marginal means			= 0.227
N — 120	3.32	3.16	2.95	C.D. at 5% level for the means			= 0.394

gradual increase in its uptake. At the first level, uptake of nitrogen was found to be non-significant when compared with zero level, but at the second level the uptake of nitrogen was significantly higher than the other two levels. The result indicated that there was difference in the uptake of nitrogen by leaves in the varieties and the type of nitrogen under test.

It may be pointed out here, that the infestation by leaf hoppers and aphids showed an increasing trend with the increase in the level of nitrogen application in the soil. This may be attributed to the fact, that the uptake of nitrogen by plants may be related to the infestation of external pests, like leaf hoppers and aphids, and have little effect on the fruit-borer infestation, which, on the other hand, is related to the varietial character alone. The Ramnagar variety had shown the maximum infestation, followed by Pusa Purple Long. Fortnightly application of Phosphamidon at 0.05 per cent concentration, reduced effectively the population of the leaf hoppers aphids and fruit-borers.

Fruit yield: The result (Table 5) indicated that the responses to the level of nitrogen and that of variety were significant at 5 per cent level. The interaction effects between the levels, varieties and types were found to be significant. The effect of Phosphamidon at 0.05 per cent conc. at 15 days' interval was found to be significant at 5 cent level but its interaction with other factors was non-significant.

The response in yield to 60 kg.N/ha was 45.7 per cent over zero level of nitrogen and at 120 kg N/ha an increase of 13.7 per cent extra yield was obtained over the first level. Among the varieties, Ramnagar gave significantly higher yield than the other two varieties, viz. Pusa Purple Long and Pusa Purple Cluster. Further, it may be seen that Ramnagar variety at 120 kg N/ha level gave the highest yield, i.e. about 15 tonnes/ha followed by the same variety at 60 kg N/ha level. Next in the order was Pusa Purple Long at 120 kg N/ha level followed by Pusa Purple Cluster at the same level of nitrogen application. Among the types of nitrogen application there was no significant difference in the yields between the treatments. However, with the Ramnagar variety ammonium sulphate nitrate, on an average, gave the highest yield followed by ammonium sulphate.

The application of Phosphamidon averaged over levels, varieties and types showed 19.6 per cent extra yield over control. As indicated earlier, Phosphamidon could effectively control the leaf hoppers, aphids and borer population, the extra yield obtained from its application may be attributed to the control of the above pests by this insecticide.

Conclusion

The experiments indicated that with the increase in the nitrogen application in the soil there was a corresponding increase in the pests infesting the leaves. The concertration of the nutrients seemed to have profound influence on the constitution of cells of the plant and thereby affect

TABLE 5—MEAN FRUIT YIELD OF BRINJAL, kg/ha

(a) Main treatment means

Treatments / Varieties	Type of N Fertilizer: Urea	Ammonium Sulphate	Ammonium Sulphate Nitrate	Level of N, kg/ha: 0	60	120	Mean
Pusa Purple Long	9178	8214	9034	7250	8855	10321	8809
Pusa Purple Cluster	8413	8111	7095	5228	8712	9679	7873
Ramnagar	10924	11685	13146	8207	12588	14960	11918
Mean	9505	9337	9759	6895	10052	11653	9533
N — 60	10391	9539	10225				
N — 120	12003	11246	11711				

(b) Sub-treatment means

Untreated	8682
Treated	10385

C.D. for the marginal means of the main treatment at 5% level = 454
C.D. for the means of the main treatment at 5% level = 786
C.D. for the sub-treatment means = 1167

the expression of the resistance in plants. The succulency of the plant might have increased with the increase in the application of nitrogen which ultimately attracted more external pests, like leaf hoppers and aphids.

But the fruit-borer's abundance was not influenced by the nitrogen content of the plant; on the other hand, it appeared to be a varietal character of the host plant. The Ramnagar variety was found to be more susceptible than the other two varieties under the trial. It requires further investigation to find out the actual cause of this preference.

The insecticide, Phosphamidon, considerably reduced the pest population in the host plants, thereby an increase of about 20 per cent of the yield was obtained from the treated plants. So, it can be said that with the increase in the use of fertilizers and improved varieties, there would be a corresponding increase in the pest population in the hosts and the requisite pest control measures could effectively control pest population to get the maximum benefit of these inputs.

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The utilization of soil and fertilizer phosphorus by crop depends considerably on the degree of base saturation and the nature of cations occupying the exchange complex, the degree of phosphate saturation of the anion sorption complex and the physico-chemical and mineralogical composition of the soil. There exists certain critical level of phosphate saturation of the anion sorption complex of the soil for the maximum utilization of fertilizer phosphorus by crop; beyond this level the utilization of fertilizer phosphorus decreases but the absorption of soil phosphorus increases. The critical level of phosphate saturation seems to be different for different soils and is dependent on a number of factors.

Effect of Degree of Base Saturation and Phosphate Enrichment on the Utilization of Soil and Fertilizer Phosphorus in Alluvial, Black and Red Soils of India

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The availability of soil and fertilizer phosphorus to a crop depends considerably on the degree of base saturation in the soil, the nature of absorbed cations on the exchange complex and the degree of phosphate saturation of the anion sorption complex of the soil. Of these factors, the effect of the degree of phosphate saturation of soil has not been demonstrated convincingly. Islam and Rahman[1] and Datta *et al*[2], no doubt, showed the importance of phosphate saturation degree of soil on the availability of soil and fertilizer phosphorus to crops. The main objective of the present investigation was to study the effect of base saturation degree of soil with respect to potassium and calcium with and without phosphate-enrichment on the availability of soil and fertilizer phosphorus to rye using labelled monocalcium phosphate in alluvial, black and red soils of India.

Experimental

Surface (0-22 cm.) soil samples were collected from Delhi (aiiuvial), Nagpur (black) and Bangalore (red) from cultivators' fields. The important characteristics of these soil samples are given in Table 1.

The 2 mm. sieved soil samples were first saturated with respect to hydrogen. 50 per cent potassium and 50 per cent calcium saturated soil samples were prepared by adding to the acid soil calculated amount of the cation required to give 50 per cent saturation of the CEC of the soil through standard solutions of potassium and calcium hydroxides respectively. The samples were air-dried and ground to pass through 2 mm. sieve. Potassium and calcium saturated soil samples were prepared by leaching acid soil with 0.04 N solution of potassium and calcium hydroxides, respectively. Excess of alkali was removed by washing with 60 per cent ethanol. Phosphate-enrich-

TABLE 1—Important Characteristics of Alluvial, Black and Red Soil

Soil Characteristics	Alluvial Soil	Black Soil	Red Soil
Soil pH (1:2.5)	8.4	8.5	5.8
Free Fe_2O_3, %	0.53	1.82	3.08
Free Al_2O_3, %	0.28	0.51	0.28
Total free sesquioxides, %	0.81	2.33	3.36
Sorbed PO_4, m.e./100 g	0.10	0.05	0.29
Anion-sorption capacity (ASC) m.e. PO_4/100 g	7.76	17.46	19.88
Olsen P, kg/ha	10	Trace	Trace
C.E.C., m.e./100 g	7.87	41.17	4.61
Soil texture	Loam	Silty clay	Clay
Mineralogical composition of clay fraction:			
1. Montmorillonite	Traces	Dominant	—
2. Illite	Dominant	Traces	Traces
3. Kaolinite	—	Traces	Dominant

TABLE 2—IMPORTANT CHARACTERISTICS OF THE SOILS AFTER CATION-SATURATION AND PHOSPHATE-ENRICHMENT

Cation System	With Phosphate-enrichment				Without Phosphate-enrichment			
	1	2	3	4	1	2	3	4
Alluvial soil								
H-soil	34.0	5.18	66.8	4.0	2.6	0.60	7.7	5.0
K-soil	30.0	2.74	35.3	8.1	2.4	0.33	4.3	9.3
Ca-soil	40.0	1.02	13.2	7.7	0.8	Trace	—	8.5
50% K-soil	31.0	4.45	57.4	5.0	2.3	0.89	11.5	6.1
50% Ca-soil	40.0	4.11	53.0	4.7	2.3	0.48	6.2	5.5
Black soil								
H-soil	23.0	2.90	16.6	3.4	0.8	0.97	5.6	4.3
K-soil	32.0	1.65	9.5	8.5	Trace	0.28	1.6	8.6
Ca-soil	32.5	0.12	6.9	7.6	Trace	Trace	—	8.6
50% K-soil	26.0	5.71	32.7	4.4	0.8	0.64	3.7	4.5
50% Ca-soil	30.0	1.81	10.4	4.4	0.8	0.27	1.5	4.3
Red soil								
H-soil	29.0	5.52	27.8	3.6	0.2	0.34	1.7	4.4
K-soil	24.0	5.96	30.0	8.7	0.2	0.29	1.5	9.5
Ca-soil	28.8	1.84	9.3	8.2	0.3	0.10	0.5	8.3
50% K-soil	27.0	5.42	27.3	4.0	0.4	0.45	2.3	5.0
50% Ca-soil	30.0	5.96	30.0	4.0	0.2	0.48	2.4	5.0

Remarks: 1. Olsen P, mg./100 g., 2. Sorbed PO_4, m.e./100 g., 3. Saturation of ASC of soil, % and 4. Soil pH.

ment of all the cation-saturated soil samples was done by adding 200 mg. P_2O_5/100 g. soil through a standard solution of phosphoric acid keeping the soil to solution ratio 1:1. The samples were air-dried. The important characteristics of the cation-saturated and phosphate-enriched soil samples are given in Table 2.

Rye was grown as indicator crop for 18 days by Neubauer's bioassay method. Phosphorus was added at the rate of 4.5 mg./100 g. soil through a standard solution of labelled monocalcium phosphate, A basal dose of nitrogen (50 kg/ha) was applied to every pot through a standard solution of ammonium nitrate.

Soil pH was determined in a soil-water suspension of 1:2.5 by Beckman pH meter. Free sesquioxide was estimated by Mackenzie's method. Available phosphorus was determined by Olsen's method.[4] Sorbed phosphate, anion sorption capacity (ASC) and CEC were determined as described by Piper.[5] Soil texture was determined by the International Pipette method. Mineralogical composition of clay was studied by x-ray diffraction technique.

Oven-dried plant samples were analysed for total phosphorus after digesting in triacid mixture of perchloric, sulphuric and nitric acids (1:2:9) by Koening and Johnson's[6] method. The estimation of P^{32} in plant samples was done by Mackenzie and Dean's[7] method. The percentage of fertilizer phosphorus utilized by plants was calculated by isotopic dilution method.

The data were analysed statistically. The experimental design was C.R.D. having two replications. The details of the treatments are given in Table 3.

Results and Discussion

The results of this experiment have been presented in Tables 3 and 4. Table 3 gives the combined effect of the different factors on the dry weight of plants, percentage utilization of fertilizer phosphorus and uptake of soil phosphorus by rye. Table 4 reveals the main effect of the different factors on the same characters.

It is evident from Table 4 that the degree of base saturation of soil and the nature of cations occupying the exchange complex of soil colloid exert significantly different effect on the utilization of fertilizer phosphorus by rye. The main effects of cations were found to be in the following order: K-soil > Ca-soil > 50 per cent Ca-soil > 50 per cent K-soil > H-soil. It is interesting to note that

TABLE 3—EFFECT OF PHOSPHATE-ENRICHMENT AND BASE SATURATION DEGREE OF SOIL ON THE DRY WEIGHT OF PLANTS, PERCENTAGE UTILIZATION OF FERTILIZER AND UPTAKE OF SOIL PHOSPHORUS

Cation System	With Phosphate-enrichment			Without Phosphate-enrichment		
	Dry Wt., g./pot	Utilization of Fert. P, %	Uptake of soil P, mg./pot	Dry wt., g./pot	Utilization of Fert. P, %	Uptake of soil soil P, mg./pot
			Alluvial Soil			
H-soil	1.76	23.3	9.5	1.75	28.7	5.6
K-soil	2.47	46.6	19.3	2.11	47.7	6.0
Ca-soil	1.83	33.2	13.4	2.38	35.2	3.6
50% K-soil	2.21	33.1	13.2	1.95	34.0	2.9
50% Ca-soil	1.55	24.6	7.4	2.45	38.4	3.2
			Black Soil			
H-soil	2.16	0.9	1.7	1.47	0.4	0.7
K-Soil	1.94	19.2	9.7	2.40	7.7	3.5
Ca-soil	2.19	26.1	12.2	2.19	14.9	1.6
50% K-soil	2.25	16.3	7.0	1.82	7.7	0.1
50% Ca-soil	2.55	19.5	9.7	1.99	9.1	0.9
			Red Soil			
H-soil	1.54	13.6	6.2	1.71	5.3	0.8
K-soil	2.52	33.0	15.7	2.07	8.5	1.0
Ca-soil	1.96	26.1	12.3	2.19	10.2	0.9
50 % K-soil	1.74	20.7	8.8	1.98	10.1	1.5
50 % Ca-soil	1.78	24.0	12.3	1.90	16.5	1.4
C.D. (5%)	NS	2.5	1.6			
C.D. (1%)	—	4.0	2.8			

NS—Not significant

the uptake of soil phosphorus as well as the fertilizer phosphorus utilization by rye increased with increasing degree of base saturation of soil irrespective of the nature of cations occupying the exchange complex. The dry weight of plants also showed almost similar trend.

The results of the present investigation apart from confirming those of Birch[8,9] provide evidences of the higher physiological availability of the phosphorus associated with adsorbed potassium and calcium at the saturation level of CEC of the soil. The less utilization of fertilizer phosphorus in acid-soils is due to the fact that in base unsaturated soils fertilizer phosphorus immediately becomes a part of the colloidal micelle and is non-diffusible. The native phosphorus also remains as a part of the amphoteric complex of soil and is therefore less available to plants. At 50 per cent level of base saturation of CEC, part of the applied phosphorus which remains in combination with adsorbed cations becomes easily accessible to plants while the fraction of phosphorus which forms a part of the amphoteric complex of soil remains in a difficultly available form. The availability of soil and fertilizer phosphorus in such soils is possibly controlled by the dominant fraction of these two components which again is dependent on the nature and properties of soils.

Phosphate-enrichment of soil has resulted in a highly significant increase in the utilization of soil and fertilizer phosphorus by rye (Table 4). It has, however, failed to produce any significant effect on the dry weight of plants.

The results are in good agreement with the observations made by Datta *et al*[2] and Islam and Rahman[1]. The observed effect can be explained by assuming that partial saturation of the anion-sorption complex of the soil is essential in order to keep the soil as well as the fertilizer phosphorus in readily accessible form. There is a possibility of the existence of a critical phosphate saturation degree of soil below which the fixation of applied phosphorus is encouraged. This critical level is different for different soils and is mainly dependent on the mineralogi-

TABLE 4—MAIN EFFECT OF BASE SATURATION DEGREE, PHOSPHATE-ENRICHMENT AND SOIL ON THE DRY WEIGHT OF PLANTS, PERCENTAGE UTILIZATION OF FERTILIZER PHOSPHORUS AND UPTAKE OF SOIL PHOSPHORUS BY RYE

Main Effect of Base Saturation Degree

	H-soil	50% K-soil	K-soil	50% Ca-soil	Ca-soil	C.D. 5%	C.D. 1%
Dry weight, g./pot	1.73	2.00	2.25	2.00	2.12	0.20	0.27
Fertilizer P Utilization, %	12.0	20.3	27.1	22.0	24.3	1.0	1.4
Uptake of Soil P, mg./pot	4.1	5.6	9.2	5.8	7.3	0.6	0.9

Main Effect of Phosphate-Enrichment

	With Phosphate Enrichment	Without Phosphate Enrichment	C.D. 5%	C.D. 1%
Dry weight, g./pot	2.03	2.00	Not Significant	
Fertilizer P Utilization, %	24.0	18.3	0.7	0.9
Uptake of Soil P, mg./pot	10.5	2.2	0.4	0.6

Main Effect of Soil

	Alluvial Soil	Black Soil	Red Soil	C.D. 5%	C.D. 1%
Dry weight, g./pot	2.02	2.10	1.94	Not significant	
Fertilizer P Utilization, %	34.5	12.2	16.8	0.8	1.1
Uptake of Soil P, mg./pot	8.4	4.7	6.1	0.5	0.7

cal and physico-chemical composition of soil. Above this critical level of saturation however, the fertilizer phosphorus utilization falls gradually but the uptake of soil phosphorus increases as can be seen in alluvial soil (Table 3).

The fall in the utilization of fertilizer phosphorus by rye can be explained by assuming that the critical phosphate staturation degree in alluvial soil lies in the close vicinity of the phosphate saturation degree of the cation-saturated soils prior to phosphate-enrichment. From Table 2 it can be seen that the phosphate saturation degree in the alluvial soil prior to phosphate-enrichment is comparatively higher in all the cation systems than in the black and red soils. With phosphate-enrichment, the phosphate saturation degree increased considerably in alluvial soil due to its low ASC. Such higher level of phosphate saturation decreased significantly the fertilizer phosphorus utilization in some of the cation systems but encouraged the uptake of soil phosphorus by crop as more soil phosphorus is liberated to the solution phase due to its low bonding energy. Thus, it appears from the results that plants absorb preferentially more soil phosphorus as compared to fertilizer phosphorus when the former exists in a readily accessible form which again is dependent on the critical phosphate saturation level of soil.

The behaviour of soils in the release of soil and fertilizer phosphorus to plants can also be seen from Table 4. The maximum absorption of soil and fertilizer phosphorus by rye was observed in alluvial soil followed by red and black soils. The differences between the soils were highly significant. The dry weight of plants was found to be at par in all the soils.

The superiority of the alluvial soil over the red and black soils is possibly due to its low free sesquioxide content and due to the presence of illite as dominant mineral in the clay (Table 1). These two factors are mainly responsible for the low ASC of alluvial soil and consequently the phosphorus fixation problem in this soil is not so acute. The red and black soils have got high free

sesquioxide content and, therefore, the utilization of applied phosphorus was comparatively less in these soils because of more fixation. The superiority of the red soil over the black soil is possibly because of its low surface area due to the presence of kaolinite as the dominant clay mineral. The presence of montmorillonite as dominant clay mineral in the black soil is responsible for its high surface area which in conjunction with free sesquioxide fixed the applied phosphorus in appreciable amount. The utilization of fertilizer phosphorus was, therefore, found to be minimum in the black soil.

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The effect of varying concentration of ammonium sulphate on the thermal decomposition of ammonium nitrate has been studied thermogravimetrically at 245°C. The weight-loss of ammonium nitrate containing 1 per cent by weight of ammonium sulphate is found to be more than that of pure salt. The extent of decomposition gradually decreases as the concentration of ammonium sulphate is increased and reaches a constant value when the concentration is around 20 per cent. The results are discussed.

Effect of Ammonium Sulphate Concentration on the Thermal Decomposition of Ammonium Nitrate

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The effect of ammonium sulphate on the thermal decomposition of ammonium nitrate is of considerable importance as both these fertilizers are often present in multi-nutrient formulations. Double salt (ammonium sulphate-nitrate) containing equimolar proportion of ammonium sulphate and ammonium nitrate is considered entirely a safe product as far as its processing, transportation, storage and handling are concerned. Surprisingly, little attention has been paid to the decomposition characteristics of ammonium nitrate in which smaller proportion of ammonium sulphate is present. Barclay and Crewe[1] carried out thermal decomposition studies of ammonium nitrate containing ten per cent by its weight of ammonium sulphate at 240°C. They noticed that the rate of decomposition of ammonium nitrate with 10 per cent ammonium sulphate is decreased in the initial stages and after 6 hours the rate of decomposition is comparable to that of pure salt.

In the present communication the effect of varying concentration of ammonium sulphate on the thermal decomposition characteristics of ammonium nitrate is studied thermogravimetrically at 245°C.

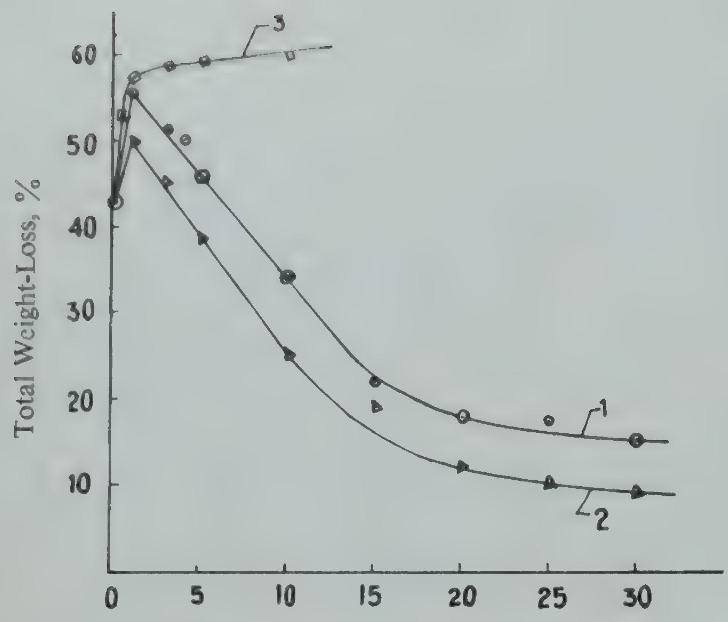
Experimental

All the chemicals used were of analytical grade. The thermogravimetric studies were carried out as reported earlier[2] and the weight-loss determined by heating the samples on an oil bath for 4 hours at 245 $\pm$1°C.

Results and Discussion

The results of thermogravimetric studies on samples of ammonium nitrate and ammonium sulphate at 245°C for 4 hours duration are shown in Fig. 1. As is evident from the graph the extent of loss in weight of ammonium nitrate is more with 1 per cent ammonium sulphate by weight of ammonium nitrate present in it. The extent of decomposition or weight-loss decreases gradually with the further increase in the concentration of ammonium sulphate. When the ammonium sulphate concentration reaches to 6.5 per cent level, the rate of decomposition is same as that of pure ammonium nitrate; with still further increase in ammonium sulphate concentration, the extent of decomposition is reduced progressively and reaches a constant value when the concentration of ammonium sulphate is around 20 per cent.

It is generally believed that addition of ammonium sulphate to ammonium nitrate causes inhibition in the rate of decomposition of the latter. This is attributed to the fact that ammonium sulphate, when heated, evolves ammonia as one of the products, which inhibits the further decomposition of ammonium nitrate in common with other ammonia liberating substances, viz. urea, zinc oxide and calcium carbonate, etc. The increase in the



Salt Added, % to the Wt. of Ammonium Nitrate

Fig. 1—Thermogravimetric Studies on Ammonium Nitrate and Ammonium Sulphate at 245°C for 4 Hours

1. Ammonium Nitrate + Ammonium Sulphate
2. Ammonium Nitrate + Potassium Sulphate
3. Ammonium Nitrate + Ammonium Hydrogen Sulphate

extent of decomposition of ammonium nitrate at lower concentration of ammonium sulphate may be due to following reactions:

$$NH_4^+ + SO_4^{2-} \rightleftharpoons NH_3 + HSO_4^- \quad \text{(i)}$$

$$HSO_4^- + NO_3^- \rightleftharpoons HNO_3 + SO_4^{2-} \quad \text{(ii)}$$

The reaction (i) suppresses the rate, whereas the reaction (ii) increases the rate. The fact that bisulphate ion increases the rate is amply demonstrated by curve 3 (Fig. 1) which shows the progressive increase in the decomposition of the nitrate, which reaches a constant value. Barclay and Crewe[1] also observed the increase in the rate of decomposition of ammonium nitrate in presence of potassium bisulphate but they concluded that bisulphate ion is not sufficiently acidic to cause the reaction (ii). The strange behaviour of acceleration of decomposition reaction in presence of 1 per cent by weight of ammonium sulphate and the acceleration of decomposition reaction in presence of ammonium bisulphate which tends to reach a constant value with the increase in bisulphate concentration can be explained on the basis of reactions as represented by equations (i) and (ii). When ammonium sulphate or bisulphate concentration in the ammonium nitrate melt is low, the accelerating effect of ammonium sulphate or bisulphate is largely due to the reaction (ii). The sulphate ion produced in the reaction in turn inhibits the decomposition of ammonium nitrate with the liberation of ammonia [reaction (i)] but the accelerating effect of nitric acid predominates.

When the bisulphate concentration in the system goes up either on account of the decomposition of ammonium sulphate or increase in the concentration of bisulphate ion, the following reaction is likely to occur:

$$HSO_4^- + HSO_4^- \rightleftharpoons H_2SO_4 + SO_4^{2-} \quad \text{(iii)}$$

The sulphate ion in turn reacts with ammonium ion [reaction (i)] with the liberation of ammonia, which inhibits the further decomposition of ammonium nitrate. The sulphuric acid formed in reaction (iii) may react with ammonia present in the system and give rise to ammonium sulphate and thus the above sequence of reactions continues.

The similar nature of the curve is obtained with ammonium nitrate-potassium sulphate system as the ions participating in reactions (i), (ii) and (iii) are all present. The decrease in the rate with potassium sulphate may be due to the decrease in ammonium ion concentration, which is known to catalyse the thermal decomposition of ammonium nitrate.[3]

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The standard Fluorescent Indicator Adsorption method of analysis of light petroleum distillate is not applicable to heavy, viscous distillates. Analysis of a typical gas oil sample is described here by extension of the existing technique, incorporating the following modifications: (a) a modified eluent consisting of a binary mixture of diethylene glycol and isopropanol, (b) a suitable diluent for gas oil, (c) a modified separating column, (d) pretreatment of high absorption capacity silica gel for use as adsorbent and (e) modification of the analytical technique.

A Modified Fluorescent Indicator Adsorption Method for Analysis of Types of Hydrocarbon Present in Gas Oil

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The FIA method[1] of analysis of naphtha and light petroleum distillates for the determination of volume composition of aromatics, olefins and saturates is not suitable for the heavier fractions, viz. gas oils, having high viscosity since the fluorescent bands are not distinct due to poor resolution. Griffith[2] applied the acid adsorption method and Mair[3] separated the fractions by adsorption over silica gel but these methods were not found satisfactory for routine analysis. It was therefore thought necessary to modify the existing techniques for developing a method suitable for the types of hydrocarbons analysis of gas oils.

TABLE 1—General Characteristics of Gas Oil Sample from I.O.C., Barauni Refinery

Aniline point, °C	..	58
Sulphur content, % by wt.	..	0.65
Viscosity, Cp	..	6.0
Distillation (ASTM 86/66, IP 123/63)		
IBP °C	..	250
50% distillate at °C	..	290
90% distillate at °C	..	325
FBP, °C	..	360

Modification of FIA Method

The FIA method of analysis in the case of heavy distillates created difficulties—the high viscosity of the sample did not permit the displacement of aromatics and waxy paraffins resulting in poor and incomplete separation in the glass column and mixing of the eluents with the sample. To surmount some of these difficulties Knight and Groennings[4] recommended the use of a modified column with a narrow separator section and low pressure so as to reduce the tendency of the eluent to mix with the sample. The efficiency of separation was somewhat improved by allowing a longer transient time.[5]

In order to overcome the difficulties in the separation of the types of hydrocarbon present, the FIA method as applicable to the light petroleum distillates has been modified in this study to suit the analysis of gas oil. The modifications carried out consisted of the following.

(a) *Use of a Modified Eluent*: The types of hydrocarbon analysis of gas oil distillate was carried out by FIA method using different binary and ternary eluent compositions. In some of the cases, the separation and displacement of olefins and saturates were possible but the aromatics were not displaced satisfactorily owing to the viscous nature of the sample. Of the various eluent mixtures of different compositions tried, the one consisting of a binary mixture of diethylene glycol and isopropanol in the ratio 3:7 v/v and having a viscosity of 6.5 Cp gave a very good separation. With this eluent mixture, the displacement of aromatics along with olefins and saturates was almost complete. The use of diethylene glycol was responsible for: (i) increasing the viscosity of the eluent to facilitate the displacement of the heavier fraction of the gas oil so that there was much less mixing of the eluent with the sample, and (ii) increasing the

polarity of the eluent composition to facilitate the desorption of aromatics more effectively and completely.

(b) *Use of a Suitable Diluent for Gas Oil*: As gas oil is sufficiently viscous to allow free flow of polyaromatics and waxy paraffins, the use of a suitable diluent was found essential. The gas oil sample was diluted with equal volume of iso-octane and then used for FIA method of analysis. The introduction of as small as 0.2 ml. of the diluted sample into the charger section of the glass column gave a good separation of the types of hydrocarbon over the analyser section. A higher concentration of the sample in the charger gave poor resolution of the constitutents.

(c) *Use of a Modified Column*: The glass column used in the ASTM Standard D-1319-65 T method was found unsuitable for analysis of the heavier distillates. The column was, therefore, modified, and in the modified column the length of the separator section was increased from 190 to 300 mm. so as to allow a longer separating section. Wider cross-section area of the separator section causes channeling of the eluent, bypassing the sample without effecting separation. To overcome this difficulty, the internal diameter of the separator was reduced from 5 to 3 mm.

(d) *Use of a Modified Adsorbent Silica Gel*: The high adsorption capacity chromatographic grade silica gel (mesh size 100-200 BSS), developed in this laboratory[6,7] was used after a pretreatment as an adsorbent in packing the glass column in the analysis of gas oil.

(e) *Modified Technique of Analysis*: The modified glass column (Fig. 1) was packed with the pretreated and

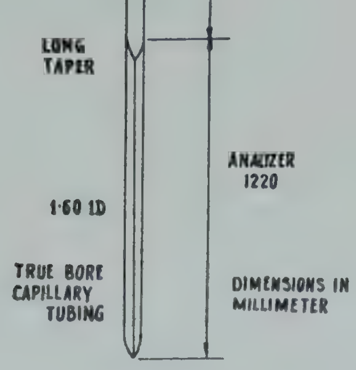

Fig. 1—Fluorescent Indicator Adsorption Column for Gas Oil Boiling Range

activated silica gel[6] with constant tapping until the separator section was half full. A sufficient quantity of dyed gel was then added so as to form a layer of 20 mm. The charger section was then filled to half its length with the silica gel and 0.2 ml. of the gas oil sample (diluted with equal volume of iso-octane) was then introduced with the help of a syringe. The remaining part of the charger section was then filled with a binary mixture consisting of diethylene glycol and iso-propanol (3:7 v/v) as eluting agent. A positive pressure or suction of 1 to 2 psig was applied to the column. When the liquid front entered the analyser section, the pressure/vacuum was released. On attaining equilibrium, the percentage composition of the types of hydrocarbon was calculated as follows:

Aromatics/Olefins volume, %

$$= 200 \times \frac{\text{length of the respective zone, mm.}}{\text{total length of the zones, mm.}}$$

The percentage composition of the saturates (paraffins and naphthenes) v/v was calculated by difference.

Results and Discussion

The analysis of several batches of gas oil from the Indian Oil Corporation's Barauni Refinery for the types of hydrocarbon analysis has been carried out by the above modified technique (Table 2).

In view of the finding that longer transient time improves the efficiency of separation,[5] a maximum time of 12 hours was allowed for the separation of the constituents in the modified technique. However, such a long contact time is likely to change the composition of olefins due to the catalytic activity of silica gel giving rise to erroneous results. It has been found in the laboratory[7] that for high adsorption capacity silica gel, the ideal contact time without involving any polymerization effect on the olefins is about 3 hours. In order to maintain the transient time within the above limit, an increase in viscosity of the eluent and dilution of the sample is essential. Only mild positive pressure/vacuum was applied to the glass column for effecting a good separation. The deviations noticed in the case of application of positive pressure from the top of the column or suction (vacuum applied from the bottom of the column) were well within the limits of experimental error when the readings were noted after attainment of equilibrium. The non-hydrocarbon compounds present, viz. sulphur, nitrogen and oxygen compounds, in the gas oil also got separated along with the aromatic compounds and hence the percentage v/v of total aromatics value includes

TABLE 2—TYPES OF HYDROCARBON ANALYSIS OF DISTILLED GAS OIL BY MODIFIED FIA METHOD

Sl. No.	Sample	Boiling range, °C	Composition %, v/v		
			Aromatics	Olefins	Saturates (P+N)
1.	Distilled gas oil	250-360	30.0	5.0	65.0
2.	Intermediate boiling range fraction of gas oil	240-300	28.0	5.5	66.5
3.	-do-	250-270	20.4	5.5	74.1
4.	-do-	275-290	26.2	4.6	69.2
5.	-do-	290-300	30.4	2.9	66.7
6.	Cracked gas oil fraction	286-314	36.0	6.0	58.0
7.	-do-	314-337	32.0	6.0	62.0
8.	West Texas Gas oil*	220-330	23.0	6.0	71.0

Note: * The values against Sl. No. 8 are reported by Knight and Groennings.[4]
The values against Sl. Nos. 6, 7 and 8 are meant for comparison.

values for these compounds as well as those for polyaromatics.

The analysis figures of intermediate boiling range fractions of gas oil indicates a progressive increase in aromatics content with corresponding decrease in the higher intermediate boiling range fractions of gas oil. The high sulphur content (0.65% by weight) in gas oil precludes its direct use for catalytic reformation/gasification processes unless the sulphur content is considerably reduced by hydrodesulphurization.

Conclusion

The modified FIA method, based on adsorption chromatography, offers a suitable and simple procedure for types of hydrocarbon analysis of heavy petroleum distillates such as gas oil.

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A detailed study of the mineralogy and genesis of clays of Bhuj Series revealed the presence of kaolinite, montmorillonite, illite and halloysite. The clay minerals are the alteration products of granitic rocks, which form the source area of the clastic sediments.

Mineralogy and Genesis of Clays of Bhuj Series in Central Kutch, Gujarat

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Introduction

During a detailed sedimentological study, one of the authors (A.T.B.) collected a few samples from the three different clay beds occurring in the sedimentary rocks in and around Bhuj city. These rocks are placed in between Jurassic and the lower part of the Cretaceous in the Kutch stratigraphy. The Bhuj Series is underlain by the Katrol rocks in the north while in the east they are overlain by the Deccan Traps.

The rocks of the Bhuj series are made up of multi-coloured sandstones and shales with occasional inter-calated clay bands. Sandstones form nearly 70 per cent of the sequence and exhibit varied textural and petrographic characters. The most typical variety of the Bhuj sandstones is snow white in colour, somewhat micaceous and friable but some varieties are pinkish brown due to the presence of ferruginous material. At some localities, the sandstone is gritty and grades upwards into a fine-grained sandstone followed by sandy and normal shales. A fining up cycle is, thus, discernible.

The shale and clay beds in this Series made up about 30 per cent of the sequence in the area. The shales are of numerous colours and are thin-bedded. A good number of exposures of clay were observed in and around Mizrapur, Fakirwari, south of Bhuj, and near Gada which is 5 km. east of Bhuj city. Three samples were studied for their mineralogical characters both under petrological microscope and electron microscope.

Experimental

Thin Section Microscopy: Thin sections were studied for their textural characters. In the samples 1 and 2 (Table 1) from Mizrapur and Fakirwari there are a good amount of detrital quartz and micaceous minerals embedded in argillaceous matrix. The quartz grains, angular with conchoidal fracture (Fig. 1), are cemented together by a clayey matrix. They form nearly 20 per cent of the rock and float in the matrix. A few grains show post-depositional corrosion of the detrital grains. The sorting is very poor on the whole and the grains are not having any preferred orientation. A few flakes of micaceous minerals are observed, which are also detrital in nature showing no bending or such features which indicate compaction. The sample 3 is bluish grey in colour with poor compaction. In thin section it is very finely grained and shows a lot of horizontal laminations. There is also later in-filling of brown iron oxide along certain fractures parallel to the laminations. This in-filling is following sutured pattern for a very short distance in a wavy manner. On the whole, the sorting is good. The detrital quartz grains are of silt size and form 5 to 10 per cent of the rock by volume. The detrital mica flakes are smaller thin laminae and show no evidence of post-depositional compaction.

Electron Microscopy: About 0.005 per cent of clay by weight was mixed with iso-amyl alcohol and dispersed using an ultrasonic disintegrator. Drops of this suspension were allowed to dry on an electron microscope grid covered with a carbon film. The grids were then examined under a microscope* at an electron optical

*Siemens Elmiskop IA.

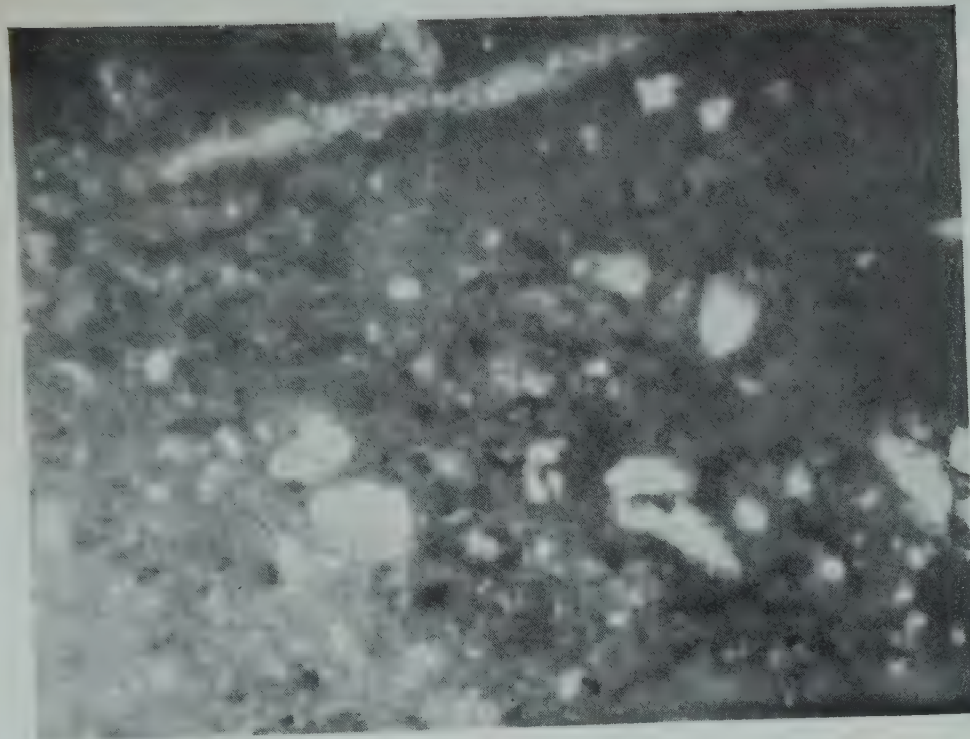

Fig. 1—Texture of the Clay (× 100)

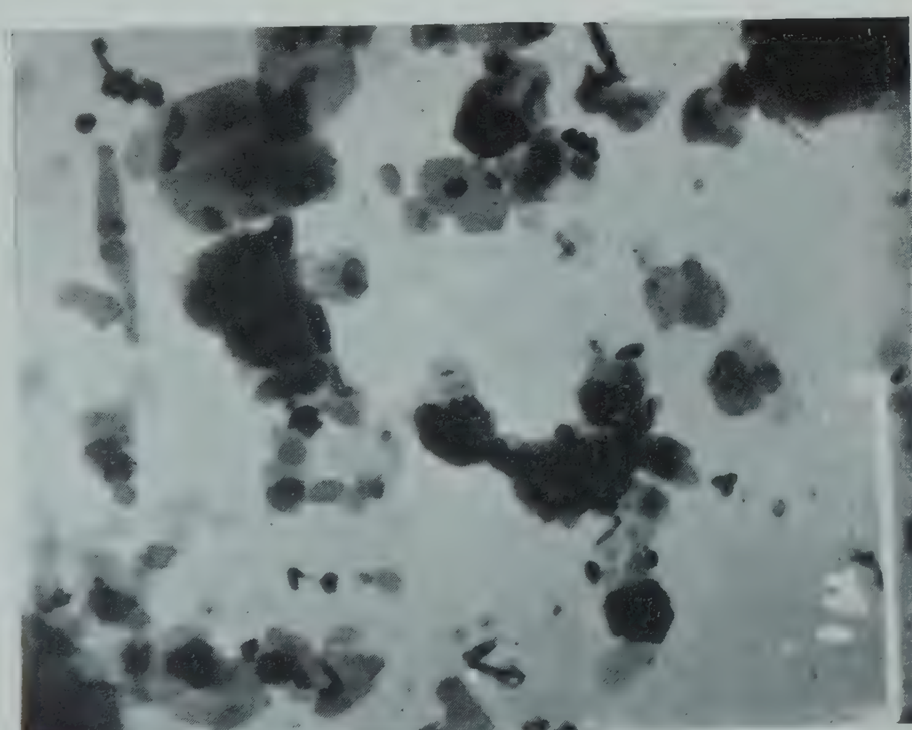

Fig. 2—Flakes of Kaolinite and Illite (× 24000)

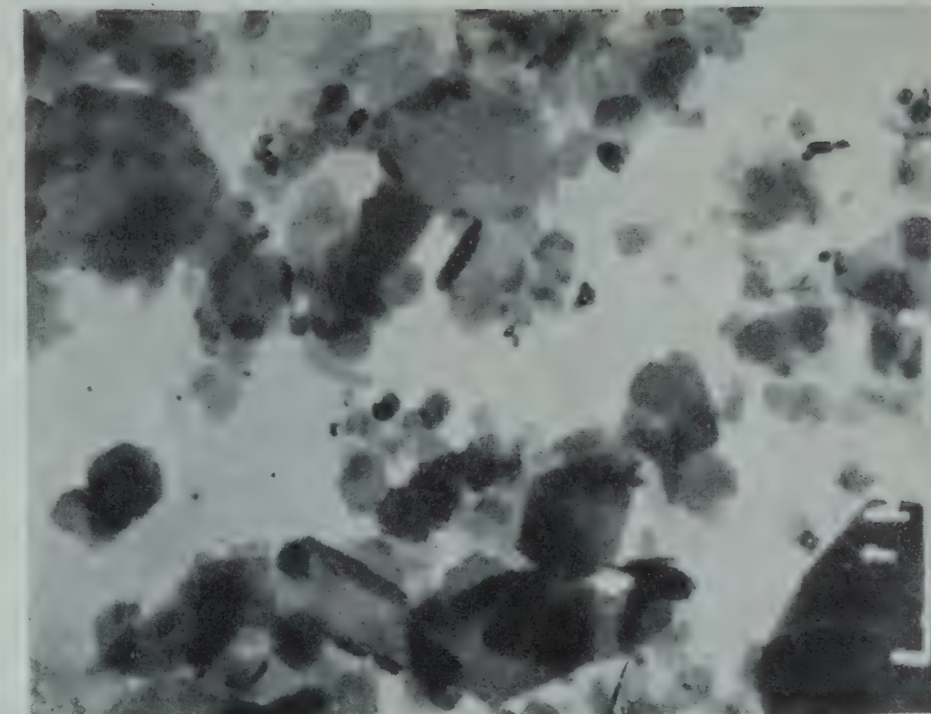

Fig. 3—Pseudohexagonal Crystals of Koalinite

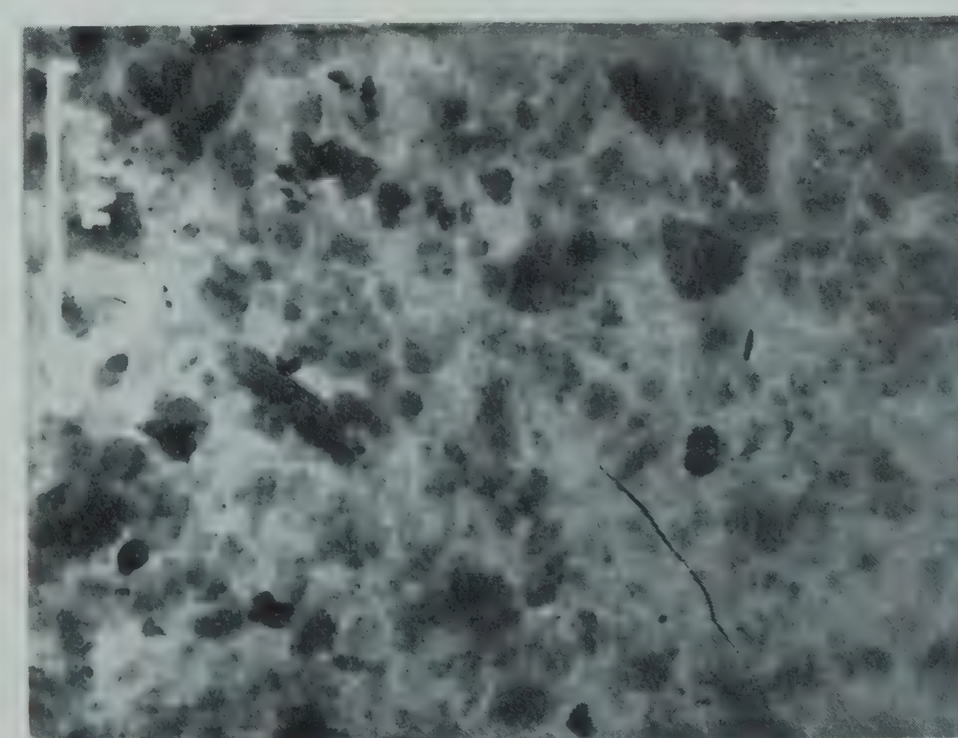

Fig. 4—Small Specks on Montmorillonite forming an Aggregate

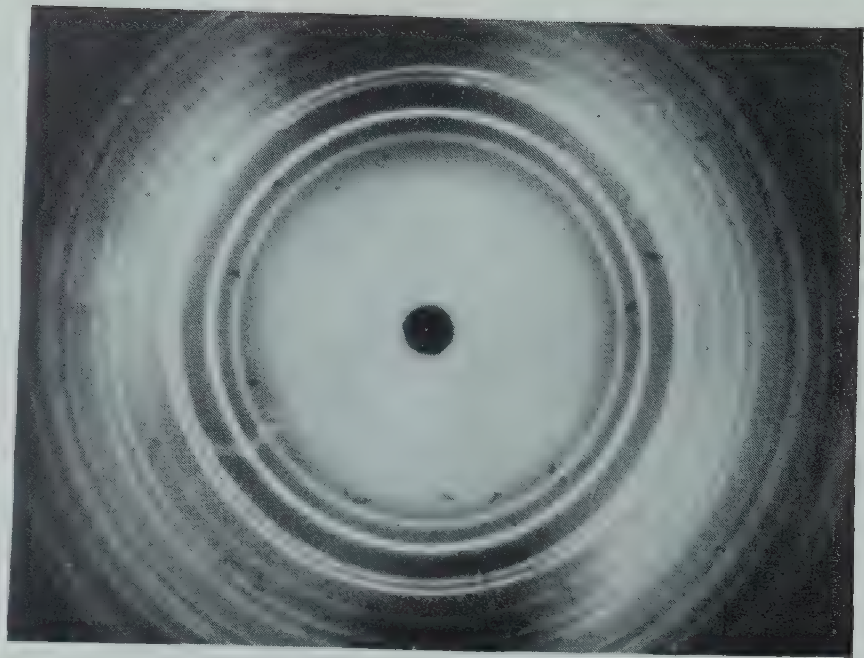

Fig. 5—Electron Diffraction Pattern of Sample 1

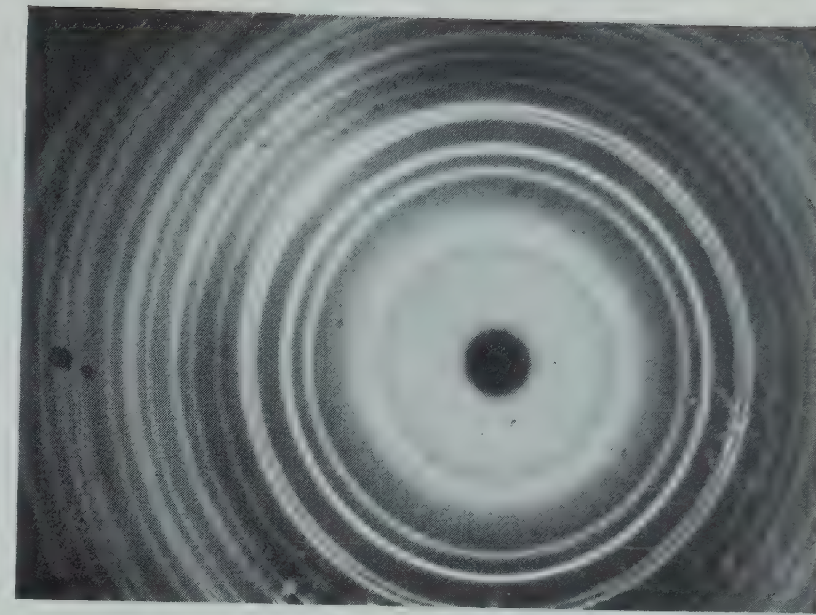

Fig. 6—Electron Diffraction Pattern of Sample 2

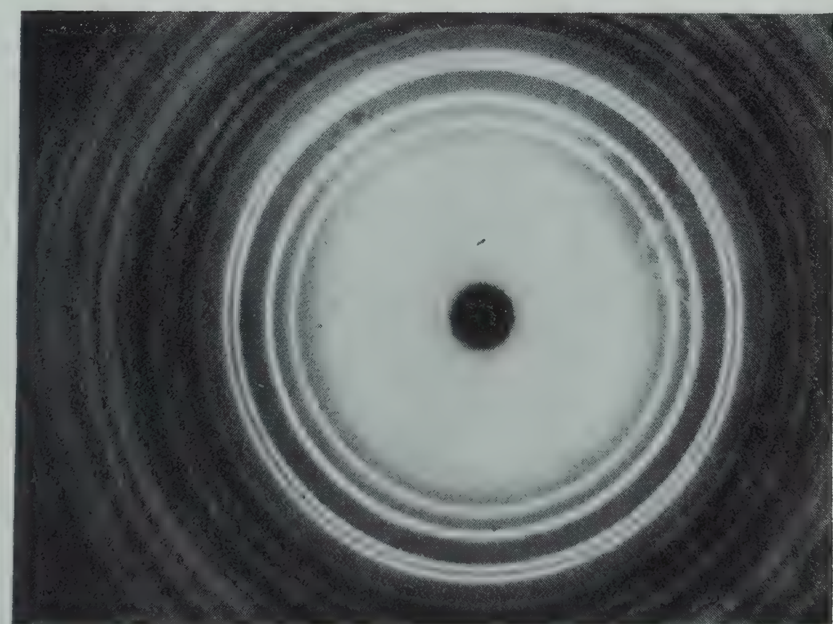

Fig. 7—Electron Diffraction Pattern of Sample 3

TABLE 1

Sample 1—Kaolinite (Montmorillonite)					Sample 2—Kaolinite (Illite—Montmorillonite)					Sample 3—Kaolinite (Montmorillonite—Kaolinite)				
Sl. No.	Index	Intensity	diam., mm.	dhkl	Sr. No.	Index	Intensity	diam., mm.	dhkl	Sr. No.	Index	Intensity	diam., mm.	dhkl
1.	131 112 200	S	18.332	2.475	1		S	11.318	4.007	1	13,20	S	17.914	2.551
2.	132,040	W	20.921	2.169	2	202	VS	18.478	2.456					
3.	150,241	S	27.070	1.676	3	133	W	20.129	2.254	2	22,04	VW	20.390	2.225
	311,311 222				4	2,0,10	S	27.409	1.655	3	31,15,24	S	26.958	1.684
4.	331	VS	30.448	1.489	5		VS with accompanying satellite line.	30.534	1.486	4	33,06	VS	30.395	1.493
5.		S	35.188	1.290										
					6		S	35.293	1.286	5	26,40	VS	35.140	1.291
6.		S	36.558	1.242	7	0.0,16	S	36.479	1.244	6	35,17,42	VS	35.140	1.291
7.		W	40.556	1.119	8		W	40.421	1.123	7	08,44	S	40.463	1.121
8.		W	44.187	1.027	9		W	44.079	1.029	8	37,28,51	S	44.018	1.030
9.		W	46.308	0.980	10		W	46.658	0.9723					
10.		VW	50.483	0.918	11		VW	50.446	0.8995	10		VW	50.380	0.9005
11.		W	52.507	0.882	12		W	52.350	0.8668	11	39.60	W	52.191	0.869
12.		W	53.497	0.848	13		W	53.312	0.8511	12		W	52.391	0.850
					14		VW	56.058	0.8093	13		VW	56.245	0.806
					15		VW	60.067	0.7553	14		VW	62.036	0.731
					16		VW	61.004	0.7433	15				
					17		W	62.671	0.7240					

magnific ion of ×24,000. Electron diffraction patterns were obta ned using the second condenser only.

In samples 1 and 2 (Figs. 2 and 3), the individual flakes of montmorillonite are extremely thin but vary considerably in the lateral extent. In sample 3 (Fig. 4), apart from the bigger two-dimensional flakes, montmorillonite also occurs in the form of small specks which tend to aggregate on the supporting film resembling in shape of thin layers. Illite in sample 2 occurs in the form of laths and angular flakes, which are thick and have undefined boundaries. Fluffy aggregates are also visible. Kaolinite is present in all the samples in the form of very well developed hexagonal crystals though there is considerable variation in the crystal sizes. In sample 1, small crystals of kaolinite seem to slip out from a big tube which could be halloysite.

Discussion

Comparison of particle size data (Table 2) obtained by electron microscopy indicated that sample 3 has the finest dispersions of the three clay samples included in the present investigations. Electron diffraction data

TABLE 2—PARTICLE SIZE RANGE OF CLAY MINERALS

Sample No.	Particle Size (Average), μ	Variation, μ	Remarks
1.	0.14	0.083-0.41	Most of the bigger particles are of kaolinite; montmorillonite particles are smaller.
2.	0.13	0.1 -0.6	Illite and kaolinite particles have comparable sizes; montmorillonite particles are smaller.
3.	0.094	0.08 -0.4	Kaolinite particles are comparatively smaller; montmorillonite is found both as large flakes and tiny specks.

(Table 1) shows that the sample 1 is predominantly kaolinite associated with significant amounts of montmorillonite, while sample 2 shows the presence of a third phase, viz. illite, besides kaolinite and montmorillonite. In sample 3, montmorillonite is the predominant phase, although traces of kaolinite are detectable.

It appears that the rocks of the Bhuj series were deposited by an easterly flowing current from a source area lying on the western side of the study area.[1] The study of the cross bedding data on the basis of about 865 observations showed a unidirectional trend with a low variance. The presence of plant fossils in these rocks and the absence of carbonate cement suggest deposition under non-marine conditions. The laminated character and multicoloured nature of the argillaceous units point to a depositional environment, which was rather quick with sediment interface fluctuating merely between oxidizing and reducing environments.

On the basis of the palaeocurrent and heavy minerals study[1], it was found that the rocks of the Bhuj Series had a source area from the Aravalli rocks, mainly made up of schists, granites and associated basic rocks.

The process of kaolinization has been discussed in a detailed manner by many workers. According to Keller[2], it is characterized by an amorphous gel phase, intermediate in stage of alteration between the parent silicate and the daughter product—a member of the kaolin group. Sand[3] has observed the feldspar is weathered directly to endellite, which is hydrated halloysite. According to Fieldes[4], the stages, viz. allophane and halloysite, are observed before the final product kaolin. Carrozzi[5] has also concluded that the association of halloysite and its relationship with kaolinite indicates the prior formation of halloysite which is partly recrystallized into kaolinite. In sample 1 the electron microscopic investigation reveals the stepping of small crystals of kaolinite from a tubular halloysite.

Kaolinite can also form directly from potash feldspar through an intermediate stage of mica.[2] Sand[3] has observed that 'the kaolinite is pseudomorphous after the mica and the basal planes of kaolinite orient, in general, parallel to those of mica'. In the present electron microscopic study, books of kaolinite were observed. They have a perfect pseudo-hexagonal outline, indicating their genesis from the secondary mica.

Conclusions

The following are the conclusions: (1) All the clay minerals of the study area are of detrital origin; (2) kaolinite has formed part of the leaching of feldspars and micas in the standing water;[6] (3) montmorillonite has been formed by the diagenetic changes from other clay minerals due to the circulation of ground waters;[7] (4) as there are no reported or known tuff beds in the Jurassic rocks or any evidence of the presence of ash beds in the Aravalli rocks which formed the source area, the volcanic origin of the montmorillonite cannot be proved. The clay beds of Bhuj Series are non-marine and contain mostly kaolinite with local occurrences of illite and montmorillonite.

Acknowledgement

The authors thank Sri K. C. Banerji for his keen interest and constant encouragement in the present study.

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[Original mss. received on Aug. 27, 1971]

An amperometric method for the estimation of nitrite in presence of nitrate has been developed. An aliquot of the nitrite solution is added to an excess of acidified urea solution containing 2 drops of osmium tetroxide as a catalyst. After half an hour, the excess urea is oxidized with excess of sodium hypobromite, excess of which is back titrated with arsenite solution amperometrically at +0.1 v *vs* S.C.E. at the rotating platinum micro-electrode. In this method, nitrate does not interfere and as small a quantity as 0.2 mg of nitrite can be estimated with an accuracy of $\pm$ 1 per cent which is comparable with other classical methods.

Estimation of Nitrite in Presence of Nitrate: A New Amperometric Method

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In spite of many available spectrophotometric methods for the determination of nitrite, only a few oxidizing agents have been reported in the literature for its volumetric estimation. Carbon and Raquet[1] determined nitrite by adding excess chlorite (ClO^-) solution and then estimating the excess chlorite by titrating with 0.05 N potassium iodide. An indirect solvent extraction method is known[2] wherein traces of nitrite are extracted as isoamyl nitrite and decomposed with sulphanilic acid; the nitrous acid liberated is determined colorimetrically. The reaction of nitrous acid with naphthylamine hydrochloride[3] is used as an absorptiometric method. Trivalent manganese[4] has been employed as an oxidant for nitrite. Zakob and Szpak[5] reported an indirect titrimetric method which consists in adding excess hydroxylamine hydrochloride and titrating the excess hydrochloride with sodium hydroxide. Hirozawa and Brasted[6] developed a new amperometeric method for the determination of nitrite with sulphamic acid in alkali chloride solution. Direct titration of nitrite with ferrocyanide, in neutral or slightly alkaline solution in the presence of zinc sulphate has been recommended[7], the end-point being the decolorization of the solution. Deshmukh *et al*[8] determined nitrite amperometrically with chloramine T solution.

In the present investigation, an amperometric method for the estimation of nitrite with urea has been developed. It is based on the fact that when sodium nitrite is added to an acidified solution of urea, nitrous acid is liberated which oxidizes urea to carbon dioxide, water and nitrogen but itself gets reduced to nitrogen and water. If a solution of nitrite is treated in the ordinary manner with urea, poor results are obtained, because the nitrite solution has first to be acidified with dilute sulphuric acid. Nitrous acid is liberated, which being unstable is partially lost. More accurate results may be obtained by adding the nitrite to an acidified solution in which urea is present in excess (the tip of the pipette containing the nitrite solution should be below the surface of the liquid during the addition), and then oxidizing the excess urea with sodium hypobromite solution and back-titrating the excess sodium hypobromite with standard arsenite solution amperometrically. Since the direct oxidation with hypobromite did not produce reproducible results, an indirect preedure for the estimation of urea by the addition of excess hypobromite with subsequent back-titration of unreacted hypobromite with sodium arsenite has been adopted.

EXPERIMENTAL

Reagents

(A) *Sodium Nitrite*: An accurately weighed quantity of the AnalaR sample was dissolved in cold deaerated water. This solution was further standardized iodometrically with thiosulphate.[9]

(B) *Urea*: Stock solution of urea was prepared from AnalaR grade sample and was standardized amperometrically with sodium hypobromite solution.

(C) *Osmium Tetroxide Solution*: This solution is pre-

pared by dissolving 1 g of osmium tetroxide in 400 ml of 0.1 N H_2SO_4 solution.

(D) *Sodium Arsenite*: E. Merck's arsenious oxide was dissolved in a minimum quantity of sodium hydroxide and neutralized with hydrochloric acid (dil.). The strength was further checked against bromate.

(E) *Sodium Hypobromite*: Preparation and standardization of sodium hypobromite were carried out by the procedure described by Kolthoff *et al.*[10]

All other reagents used were of AnalaR quality.

Apparatus

Titrations were carried out in an apparatus designed and fabricated in this laboratory[11]. Readings were taken using rotating platinum micro-electrode as the polarizable electrode. The non-polarizable reference electrode used was a saturated calomel electrode with Agar-KCl bridge.

Procedure

3 ml. of 0.05 M urea was pipetted out in a 100 ml. pyrex beaker and was diluted to 10 ml. 4 ml. of 12 N sulphuric acid was added to this solution. 5 ml. of 0.03 M sodium nitrite solution was added to this mixture by dipping the tip of the pipette inside the solution. Two drops of osmium tetroxide solution was added and the contents of the beaker were mixed thoroughly. Then the beaker was kept aside at room temperature (30°C) for about 30 minutes to ensure complete reduction of nitrous acid. 7.6 ml. of 15 N sodium hydroxide solution was added and the beaker was cooled in ice-cold water. Then an excess of sodium hypobromite solution was added to oxidize the remaining excess of urea. 0.1g. of sodium bicarbonate was added and the solution was diluted to 35 ml. The remaining excess of sodium hypobromite solution was back-titrated with standard arsenite solution. The end point was detected amperometrically. At an applied potential of + 0.1 v *vs* S.C.E., the anodic current of sodium hypobromite decreased upto the end point and then remained steady with excess arsenite solution. A blank titration was also run simultaneously. The volume of arsenite required for unreacted hypobromite was determined graphically.

RESULTS and DISCUSSION

Results of a series of experiments revealed that 2 moles of sodium nitrite are required to oxidize 1 mole of urea. Therefore the mechanism of the redox reaction may be represented as follows:

$$2H^+ + 2NO_2^- + \begin{matrix} NH_2 \\ NH_2 \end{matrix}\!\!>\!CO \rightarrow 2N_2 + CO_2 + 3H_2O$$

and the strength of the sodium nitrite solution may be calculated using the formula

$$\text{Strength of Sodium Nitrite} = \frac{\text{Volume of Urea Consumed} \times \text{Strength of Urea} \times 2}{\text{Vol. of Sodium Nitrite Taken}}$$

A series of determinations were made and the results obtained are recorded in Table 1. The observations show

TABLE 1—Determination of Nitrite by Amperometry and Iodometry Amount of Nitrite Determined, mg.

Amperometry	Iodometry
2.000	2.002
3.175	3.170
5.256	5.255
10.190	10.190
15.258	15.256
20.500	20.500

that sodium nitrite upto 0.2 mg. may be determined within ± 1 per cent accuracy. 100-fold excess of nitrate does not interfere in these determinations.

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Used-up hollow cathode lamps of zinc, lead and nickel which become useless mainly due to clean-up of the fill gas have been utilized. The vacuum of the lamp is released and fill gas (argon) at the desired pressure is maintained with a stopcock arrangement. Arsenic hollow cathode lamp is converted for copper by inserting a copper cylindrical cathode into the cathode cup and the performance of such lamps is quite comparable with that of the original ones.

Utilization of Used-up Hollow Cathode Lamp in Atomic Absorption Spectrophotometric Studies

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Introduction

One of the limitations of atomic absorption spectrophotometry is the requirement of individual hollow cathode lamps for analysis of the specific element. Such lamps are easy to operate, stable and give a high line-to-background ratio. Recently developed high intensity lamps give even better results. At present about seventy elements can be analysed by this technique and therefore a large number of lamps are required which are very costly, their price ranging from 100 to 175 dollars. The cost of the set of hollow cathode lamps, which are normally required in a research and development laboratory where assorted materials are analysed for multiplicity of elements, becomes much higher than that of the instrument itself. Hollow cathode lamps deteriorate on prolonged use either by clean-up of the fill gas or sputtering out of the cathode material and sometimes they even deteriorate in the shelf itself due to outgassing. The manufacturers give a guarantee for the lamp life, which in the present case (Perkin-Elmer make) is 6 months and the operating life is 5 ampere-hours. In countries like ours, the procurement of these lamps adds to further difficulty. It is not possible to replace the depleted lamp and add a new one on a short notice. Sometimes it also happens that the lamp gives way in the midst of an important analysis.

Demountable hollow cathode lamps have been used by several workers[1–3] as an alternative to the sealed hollow types. The cathode is made of the specific element and can be changed when desired. The lamp is connected to a vacuum pump through a pressure gauge; fill gas, generally argon, neon and sometimes helium, is continuously passed through the lamp and the flow is monitored by needle valves. The gas flow cools the system and a high current is generally required; sometimes a cooling arrangement for the cathode block and a separate power supply are needed. These demountable lamps may become indispensable due to their versatility and low cost, though they are cumbersome to use.

In the process of developing a demountable hollow cathode lamp, the clean-up lamps were tried which are practically of no use. The zinc, lead, nickel and arsenic lamps became inoperative and gave background radiation only, and to reactivate them, the polarity of the lamps was reversed and they were warmed for several hours but even then found unusable. In fabricating the demountable lamps one has to consider the cathode material, its design, geometry, cathode and anode distance and a number of other parameters. While using the used-up lamps, these parameters were not considered as the lamps are originally manufactured taking them into account. Simply a stopcock to be joined at the sealed end, a vacuum pump for evacuation and a fill gas at desired pressure are required. The materials available at hand were only used. The sensitivities obtained for zinc, lead, nickel and copper were comparable to those of original lamps.

Experimental

Used-up Perkin-Elmer zinc (Zn-Ca), lead, nickel and arsenic hollow cathode lamps, model 303 Atomic Absorption Spectrophotometer equipped with a standard burner head, a rotary vacuum pump and argon gas were used. Air-acetylene flame was used for all the studies.

Construction and Procedure: The insulating cap and the leads of zinc, lead, nickel and arsenic hollow cathode lamps were removed from the rear end of the lamps. The vacuum was released from the point they were sealed. Only in the case of conversion of the arsenic used-up lamp into a copper one, the lamp envelope was cut from the middle and a cylindrical copper cathode with an inner diam. of 5/32″ was snugly fixed into the cathode cup and was joined again. To the sealed end of each lamp, a stopcock was joined at right angle to their lengths (Fig. 1). The length of right angle joint was kept

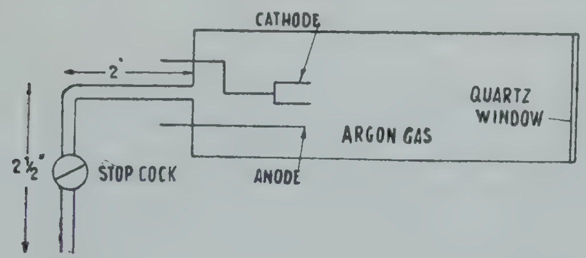

Fig. 1—Sketch Diagram of the Modified Hollow Cathode Lamp

small, so that the lamps could be mounted in the lamp-housing and its cover could also be closed. A hole was drilled at the centre of the end caps such that the conecting glass tube could pass through it. Then the caps were cut in two halves to facilitate the refixing on the lamps. The connection of the lamp connecters was changed such that it could draw current up to 50 mA from the power supply of the instrument. The leads were then connected to the lamps as in the original case and the two halves of insulating cap were fixed together as well as with lamp with the help of an adhesive.

The lamp was mounted in the lamp-house and connected to the vacuum pump with the help of pressure tubing through a three-way stopcock and a simple glass manometer. The other end of the stopcock was then connected to the argon gas cylinder which was used as fill gas as other gases (neon or helium) were not available at hand. Evacuation, flushing with argon and stabilization of current of the lamps are dealt under individual lamps. It was observed that the noise reduces as the pressure decreases. The best condition for pressure was selected by keeping watch on the energy meter. The studies were made at different slit width and current conditions.

Results and Discussion

Zinc Hollow Cathode Lamp: The sealed zinc lamp worked well in the initial period but after some use gave only the background radiation. There was a discharge in the neon filler gas but the cathode failed to glow. The polarity was reversed and the lamp was warmed up for several hours, even then the condition did not improve. Though it worked for about two years very well, it did not survive the operating life of 5 ampere-hours. During this period of operation a white silver-like film had deposited on the inner side of the lamp envelope. It was evident that lamp failed either due to decrease in the pressure of the fill gas or excessive sputtering. The complete sputtering of the zinc was not possible as the zinc-calcium intermetallic compound[4] in the cathode cavity has a high melting point, viz. 600°C.

The deteriorated lamp, tried with the original cathode in the present study, worked satisfactorily. The clean-up lamp, with the vacuum stopcock arrangement was mounted on the instrument and switched on and set for zinc analysis[5]. The lamp was evacuated, flushed with argon two or three times and finally connected to the pump again. When the lamp started glowing, the stopcock was closed and the current raised to 50 mA. In 5 min. the current dropped to 25 mA. The lamp was again put into the vacuum line and the needle of the energy-meter showed increasing energy. When the energy reached maximum, the current also went up to 30 mA, at which the stopcock was closed and the pressure tubings removed. The lamp was then ready for absorption studies. At lower currents the sensitivity increased but the fluctuation also increased. The best compromise between the gain and the current was at 25 mA. The absorption could not be adjusted to zero (with the zero adjustment knob even when the flame was not lighted). This was due to high absorption by the windows in the path of the sample beam, at lower wave length (2138Å). The windows of the photometric cover were removed and then the zero could be adjusted with zero knob itself even when the flame was on.

The working curves of zinc at various slits and at the selected current of 25 mA are shown in Fig. 2. It can be seen that a narrow slit 3 (2 Å), instead of the recommended slit 5, gives better results. The sensitivity obtained at slit 3 (2 Å) and current 25 mA is 0.026 μg/ml/1 per cent absorption, while the sensitivity of the sealed lamp is 0.04 μg/ml/1 per cent absorption (Table 1).

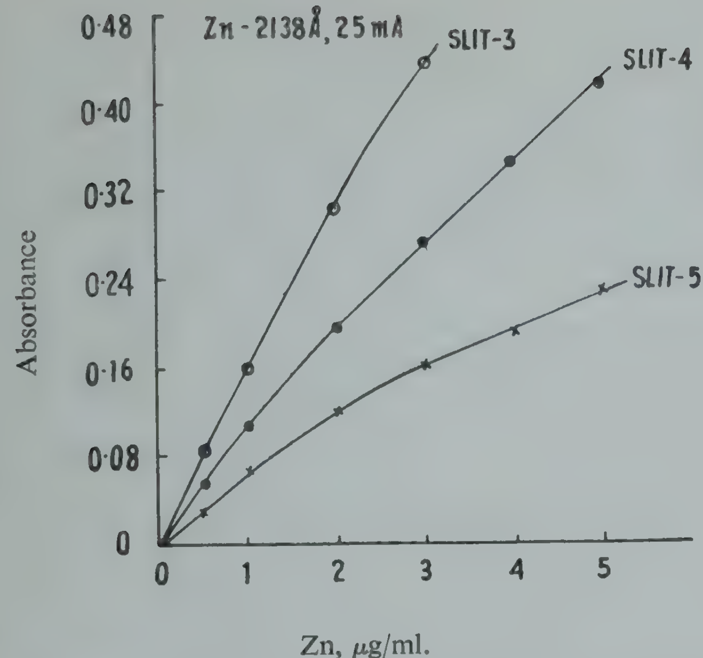

Fig. 2—Calibration Curve for Modified Zinc Lamp with Window Covers Removed

The sensitivity obtained with the used-up zinc lamp is comparable with the original one. Its intensity appears to be low which may be partly due to depletion of zinc from the cathode cavity and partly to the poor response of the photometric optics in the U/V region, due to long use. An enhancement[6] in the line intensity could be expected with neon as fill gas as it produces most intense neutral atomic line spectra. The lower slit width found suitable in the present case may be due to high current which may be causing a broadening of the line. This lamp, it appears, may work better if a continuous flow of gas is maintained as in the demountable lamp, which removes the vapours from the front of the cathode cup. For good performance, the lamp once filled required refilling and evacuation after being in use for a few hours.

Since the zinc-calcium alloy is in the cavity, the calcium absorption studies were also made but the sensitivity achieved was very poor in this case.

Lead Hollow Cathode Lamp: Lead-sealed hollow cathode lamp worked for about a year and then became inoperable. The operating life was short of 5 ampere-hours. There was a discharge in the neon gas, but the cathode did not glow. Some blackish deposit was formed on the inner side of the envelope and in the cathode cavity lead compound was still seen. The instrument was set for the study of lead as given in the analytical method[5]. The lamp with a stopcock arrangement was evacuated and flushed with argon and the stopcock was closed finally as in case of zinc lamp.

Lead 2170 Å and 2833 Å lines were used for absorption studies. The 2170 Å line is twice as sensitive as

TABLE 1—Operating Conditions of the Modified Lamps

Element	Wave Length, Å	Slit Number (Spectral band width)	Current, mA	Sensitivity Obtained, μg/ml/1% absorption	Sensitivity of Neon-filled Lamps,[5], μg/ml/1% absorption
Zn	2138 (Windows removed)	3 (2Å) 4 (7Å) 5 (20Å)	25 25 25	0.026 0.04 0.07	0.04
Pb	2170 (Windows removed)	3 (2Å) 4 (7Å)	25 25	0.54 0.88	
	2833	3 (2Å) 3 (2Å) 4 (7Å) 4 (7Å)	30 25 30 25	0.88 0.83 1.33 1.33	
	2833 (Windows removed)	3 (2Å) 4 (7Å)	30 30	0.61 1.11	
Ni	2320	3 (2Å) 4 (7Å)	22 22	0.99 0.19	0.2
	3524	3 (2Å) 4 (7Å)	22 22	0.45 0.53	
Cu	3247	4 (7Å)	20	0.11	0.15

2833 Å, but the former in the present case could not be used with the window covers due to heavy absorption. The 2833 Å line was used when windows were covered with glasses, whereas both the lines were used when the window covers were removed as in the case of zinc. The sensitivities at different current and slits has been shown in Table 1. The sensitivity at slit 3 (2 Å) is better than at the recomended slit 4 (7 Å). The sensitivity of 2170 Å line is better than that of 2833 Å but the noise is more. This may be due to argon line falling at 2170 Å and some other lines very near to it. Slavin and Manning[7] have observed that the neon-filled lamp gives a better performance than the argon-filled one. Neon gives a cleaner spectrum than argon at these wave lengths and therefore, the analysis is quiter than in the argon-filled lamp. The performance of argon-filled lamp at 2833 Å was found satisfactory. The analysis is quiter at reduced gas pressure. Once the lamp was filled it worked for a few weeks like a sealed one.

Nickel Hollow Cathode Lamp: The sealed nickel hollow cathode lamp worked nicely for about two years and then ceased to function due to clean-up.

In this lamp, the current stabilized at 22 mA and absorption studies were performed at 2320 Å. The calibration curves at slits 3 (2 Å) and 4 (7 Å) are shown in Fig. 3. As the multi-element (cobalt, chromium,

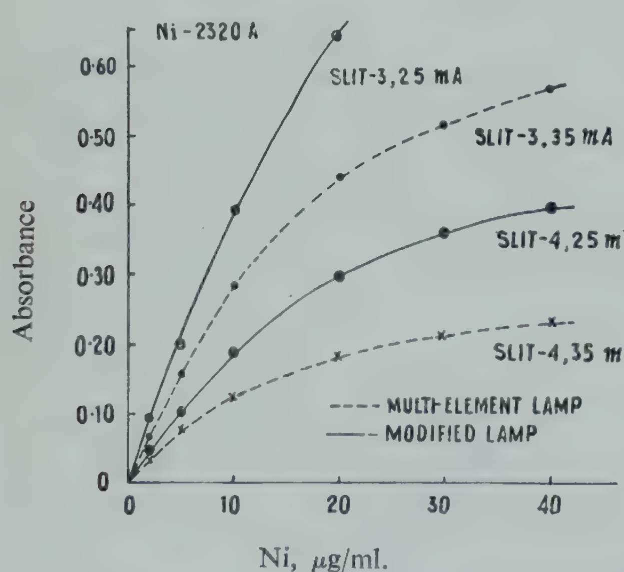

Fig. 3—Calibration Curve for Modified Nickel Lamp

copper, manganese and nickel) lamp was available, observations for nickel were taken for comparison. The calibration curves obtained with this lamp are given in the same figure. The modified used-up lamp of nickel gives higher sensitivity than the sealed multi-element lamp which was in use for quite some time. The sensitivity is comparable with the original nickel lamp[5]. The performance of nickel at 2320 Å is almost same with or without the windows covered.

The sensitivities of nickel using 3524 Å line at slits 3 (2 Å) and 4 (7 Å) are given in Table 1. The analysis at these wave lengths is very quite. The lamp once filled at the desired pressure works for several days very satisfactorily.

Copper Hollow Cathode Lamp: The deteriorated arsenic lamp could not be used again. This may be due partly to sputtering out of arsenic from the cathode cavity and partly to the poor response of the photometric optics in the ultra violet region. Air also absorbs heavily in this region. Therefore, instead of arsenic the lamp is used for copper by modifying the cathode as discussed earlier. The performance of this modified lamp is comparable with that of the original sealed copper lamp (Table 1). This suggests that the used-up lamp can be modified for any other desired element also.

Conclusion

From the present study, it is seen that the zinc, lead and nickel hollow cathode lamps, which deteriorated primarily due to gas clean-up, can be reutilized by maintaining the fill gas pressure with stopcock arrangement. The copper lamp, converted from an used-up arsenic lamp, shows that the lamp of one element can be successfully converted to another. Those adjusted for optimum pressure work for quite some time. Lead lamp was used many times during a month without purging. Their performance is quite comparable to that of the original sealed lamps.

However, the intensity of the refilled lamps, particularly of zinc and lead, was low. This may be due to replenishing of the elements from the cathode cup. In the present case, the noise was slightly more due to comparatively high gain employed. The static gas system has an advantage of being simpler than the dynamic gas system of demountable type of lamps.

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The total ammonia capacity of the plants in operation/under construction/advanced planning stage in the country amounts to 5.6 million tonnes/year, of which the FCI Ltd. accounts for an annual capacity of 2.73 million tonnes (48 per cent of total). The FCI plants based on heavy stocks are of the order of 29 per cent, on naphtha 24 per cent, on coal 22 per cent and on natural gas 10 per cent. Among the plants that are not fully in the Public Sector, more than 98 per cent capacity is based on naphtha.

An analysis has been made on the requirement of feedstock, utilities, investment costs and production costs for five plants using different feedstocks. The investment cost for the natural gas plant is the lowest followed by those of naphtha, heavy stocks and coal-based plants. The cost of production also follows the same order but with projected 1975 costs for feedstocks, the disparity in the costs of production between the plants is much less pronounced.

Feedstocks for future ammonia plants have been discussed. The foreign exchange outgo for the production of ammonia is the lowest in the case of indigenous feedstocks. The petroleum feedstocks based ammonia requires lesser amount of foreign exchange than the coal-based one, while it is the highest for the imported naphtha-based ammonia. It is possible that the off-shore crude may provide enough surplus to meet a part of the feedstock requirement for ammonia. In the event the expectations of off-shore crude prove unsatisfactory, the coal-based projects would provide adequate experience and data for further consideration of expansion of the industry based on coal for the 1978-79 programme and beyond.

Ammonia Production Based on Various Raw Materials*

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Feedstocks Used in India

In India, the feedstocks that have been used/proposed for use, for the production of ammonia, include lignite/bituminous coal, coke, coke oven gas, electrolysis of water, natural gas, naphtha, refinery gas and heavy stocks. The ammonia plants that are in operation and those under construction,/advanced planning stage, along with the feedstocks in use/planned, are given in Table 1. The total capacity of all these plants amounts to nearly 5.6 million tonnes of ammonia per year.

The ammonia production capacity of the FCI Ltd. at approximately 2.73 million tonnes per annum accounts for 48 per cent of the total production capacity in India. The daily production capacity amounts to approximately 8,000 tonnes of ammonia. The distribution of ammonia production capacity, according to the feedstock used for all plants in India, for FCI Ltd. alone and for plants other than in the fully owned public sector, is given in Table 2.

More than 50 per cent of the country's production capacity for ammonia is based on naphtha; heavy stocks account for 14 per cent of the capacity; coal accounts for about 10 per cent and natural gas for another 10 per cent. Imported ammonia represents roughly 7 per cent of the capacity. An analysis of the production capacity of FCI Ltd. shows that coal accounts for about 22 per cent, naphtha 24 per cent, heavy stocks 29 and natural gas about 10 per cent. All the three plants using heavy stocks as well as the two coal-based plants belong to FCI Ltd.

Therefore, when all the plants that are under various stages of construction go into production, FCI Ltd. would be in a better position to more thoroughly evaluate the effect of the type of feedstock on plant performance.

*Paper presented at the Second International Fertilizer Symposium held at Kiev, Ukranian SSR during Sept. 21 to Oct. 1, 1971 and later at New Delhi during Oct. 2—12, 1971.

TABLE 1—AMMONIA PLANTS IN INDIA

Location	Ammonia Capacity, te/yr.	Feedstock
FCI Ltd. Sindri	153,500	Coke/Coke Oven Gas/Naphtha
" Nangal	101,300	Electrolysis
" Trombay	115,500	Naphtha
" Gorakhpur	115,500	Naphtha
" Namrup	66,000	Natural Gas
" **Durgapur	198,000	Naphtha
" **Barauni	198,000	Naphtha
" **Namrup Expansion	198,000	Natural Gas
" **Ramagundam	297,000	Bituminous Coal
" **Talcher	297,000	Bituminous Coal
" **Haldia	198,000	Heavy Stocks
" Trombay Expansion	200,000	Imported Ammonia
" **Nangal Expansion†	297,000	Heavy Stocks
" **Sindri Expansion††	297,000	Heavy Stocks
Sub-Total	2,731,800	
FACT Alwaye	112,200	Naphtha
" **Cochin-I	198,000	Naphtha
Cochin-II	55,000	Imported Ammonia
Neyveli Lignite Corpn., Neyveli	94,000	Lignite
New Central Jute Mills, Varanasi	13,200	Coke
Hindustan Steel Ltd. Rourkela	152,800	Coke Oven Gas/ Naphtha
GSFC Ltd., Baroda	313,500	Naphtha/Natural Gas
Coromandal Fertilizers	107,300	Naphtha
EID-Parry Ltd., Ennore	19,800	Naphtha
Shriram Fertilizers, Kota	148,500	Naphtha
Indian Explosives Ltd., Kanpur	274,000	Naphtha
**Madras Fertilizers Ltd., Madras	250,000	Naphtha
Zuari Agro Industries, Goa	220,000	Naphtha
**IFFCO, Kalol	300,300	Natural Gas/ Naphtha
Dharamsey Morarji, Shevanova	120,000	Imported Ammonia
**Southern Petrochemicals, Tuticorin	363,000	Naphtha
Malabar Fertilizers, Mangalore	198,000	Naphtha
Total	5,671,400	

†In planning stage
††Of which, 90,000 te. capacity would replace existing capacity on coke, which would be discontinued.
**Plants based on centrifugal compressors.

Among the plants that are not in the fully owned public sector, more than 98 per cent production capacity is accounted for by naphtha and natural gas alone.

Processing of Feedstocks for Synthesis Gas Production

Table 3 gives the production capacity distributed on the basis of process employed for gasification of the feedstock.

The two old plants, viz. at Sindri and Varanasi, use coke as the raw material for semi-water gas generation for synthesis gas production. Low temperature purification of coke oven gas accounts for a part of the synthesis gas production at Sindri (43,000) and for a substantial production at Rourkela (100,000). Electrolysis of water is used in only one plant, viz at Nangal. Adequate power availability and heavy water production were factors for adopting the electrolysis route. Steam-reforming of naphtha and natural gas account for a major portion of the ammonia capacity (3.15 million tonnes of ammonia per year) amounting to more than 60 per cent, partial oxidation of oil accounts for (1.12 million tonnes of ammonia per year) about 21 per cent of the capacity. Plants based on oxygen gasification of bituminous coal/lignite account for about 13 per cent of the capacity.

An analysis of the capacity of FCI Ltd. shows that partial oxidation accounts for 40 per cent, steam-reforming about 27 per cent and gasification of bituminous coal about 24 per cent of the capacity.

The plants which are not fully in the public sector would obtain all their ammonia by naphtha/natural gas steam-reforming process.

Typical Schemes for Processing Feedstocks

The process schemes adopted for processing different feedstocks vary with the type of feedstock. The typical process schemes that are being adopted in the new plants are only being briefly outlined. The possibility of use of coke/coke oven gas or electrolysis* in large plants at present is considered remote.

Natural Gas and Naphtha: Desulphurized natural gas is subjected to steam-reforming at about 28-30 atm. This is followed by an auto-thermal secondary reformer where air is added to give the desired hydrogen to nitrogen (3:1) ratio in the synthesis gas. The reformed gases containing low methane content are subjected to a two-stage CO-conversion to reduce the carbon monoxide content to low levels. The gases are subsequently freed from carbon dioxide either by MEA wash or by scrubbing with activated potassium carbonate solution. The final removal of residual carbon monoxide and carbon dioxide is accomplished by methanation. The purified synthesis gas is subsequently compressed and introduced at the appropriate stage in the ammonia synthesis loop.

*Electrolysis for hydrogen production in an agro-chemical complex centred around a large atomic power generation unit is currently being discussed.

TABLE 2—FEEDSTOCK-WISE CLASSIFICATION OF AMMONIA CAPACITY IN INDIA

Feedstock	All India		FCI Ltd.		Other than Public Sector Plants	
	Ammonia, te/yr	%	Ammonia, te/yr	%	Ammonia, te/yr	%
Coke	103,200	1.8	90,000[1]	3.3	13,200	0.6
Coke Oven Gas	136,400	2.4	43,000[1]	1.6	—	—
Lignite	94,000	1.7	—	—	—	—
Bituminous Coal	594,000	10.5	594,000	21.7	—	—
Electrolysis	101,300	1.8	101,300	3.7	—	—
Naphtha	2,911,200	51.2	647,500	23.7	1,894,100	81.3
Heavy Stocks	792,000	14.0	792,000	29.0	—	—
Natural Gas	564,300	10.0	264,000	9.7	300,300	12.9
Imported Ammonia	375,000	6.6	200,000	7.3	120,000	5.2
	5,671,400	100.00	2,731,800	100.0	2,327,600	100.0

[1] Proposed to be discontinued and replaced by naphtha reformation/partial oxidation of heavy stocks.

TABLE 3[1]—PROCESS-WISE CLASSIFICATION OF AMMONIA CAPACITY IN INDIA

Process Employed	All India		FCI Ltd.		Other than Public Sector Plants	
	Ammonia, te/yr	%	Ammonia, te/yr	%	Ammonia, te/yr	%
Semi-water gas[2]	103,200	1.9	90,000	3.6	13,200	0.6
COG Separation	136,400	2.6	43,000	1.7	—	—
Electrolysis	101,300	1.9	101,300	4.0	—	—
Steam Hydrocarbon Re-forming	3,152,100	59.6	680,500	26.9	2,174,600	98.5
Partial Oxidation of Oil	1,115,400	21.0	1,023,000	40.3	19,800	0.9
Gasification of Bituminous Coal/Lignite	688,000	13.0	594,000	23.5	—	—
	5,296,300	100.0	2,531,800	100.0	2,207,600	100.0

[1] Excludes Imported ammonia

[2] Proposed to be discontinued by 1975-76

The newer large capacity plants are in single stream and employ centrifugal compressors for major services.

The process sequence in the case of naphtha feedstock is the same as that for natural gas except that the raw naphtha is subjected to a preliminary hydrodesulphurization step to remove the bulk of the sulphur. The naphtha-reforming catalyst is different and the purification section is larger due to the higher carbon content in naphtha. A typical process block diagram is shown in Fig. 1.

Heavy Stocks: The heavy oil is subjected to partial oxidation with oxygen. Pressure varies between 30 and 90 atm. Most of the old plants are designed for 28-30 atm. pressure, whereas the new plants are being designed for 55 atm. Operations at 80 atm. pressure and above has been suggested and one or two plants of large capacity at higher pressure are on stream but experience is still limited.

The raw gas is freed from carbon formed during the gasification step by scrubbing with water. The raw gases are then subjected to desulphurization using Rectisol process. The final purification for carbon monoxide removal is accomplished by liquid nitrogen wash. After the addition of pure nitrogen for correcting the hydrogen nitrogen ratio, the synthesis gases are compressed and introduced into the synthesis loop. A typical process block diagram is shown in Fig. 2.

Except for the gasifiers, the plants are largely to be in

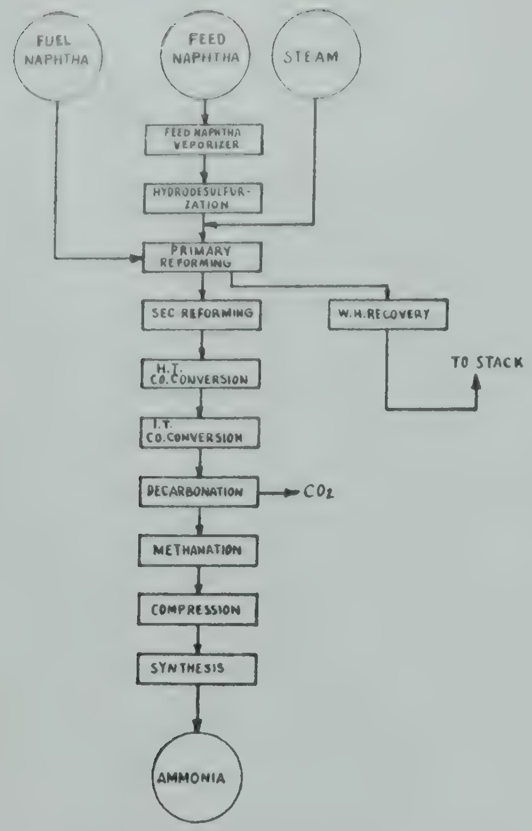

Fig. 1—Naphtha Based Ammonia Plant

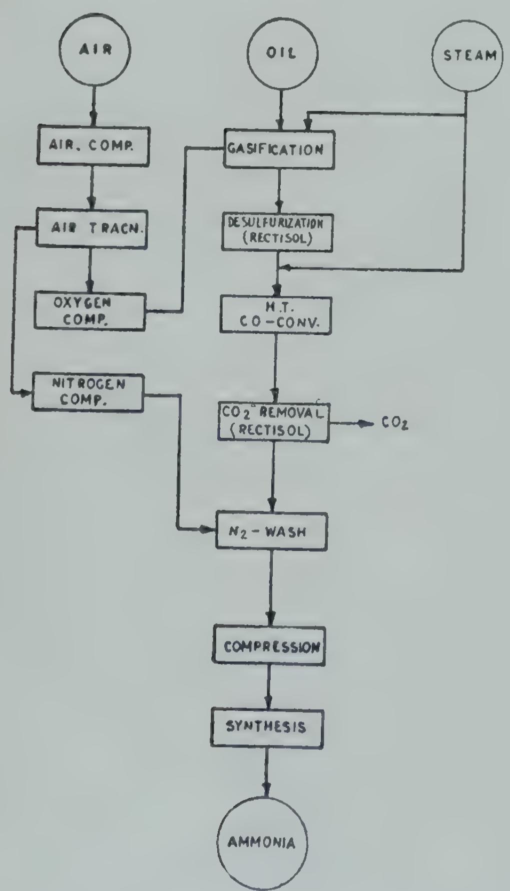

Fig. 2—Furnace Oil Based Ammonia Plant

single stream with centrifugal compressors. The planned capacity is 600/900 te ammonia/day.

The main differences between the partial oxidation of heavy stocks plants when compared to the naphtha steam-reforming plants are that in the former (i) large air plant required for the production of 98 per cent oxygen and pure nitrogen; (ii) auto-thermal non-catalytic single stage gasification step; and (iii) bigger capacity purification unit.

Coal: Pulverized coal in suspension is gasified with oxygen at slightly above atmospheric pressure. Koppers-Totzek gasifiers are being adopted. The raw gas after heat recovery is subjected to a purification step which finally includes an electrostatic precipitator to reduce the dust content to low levels. The gas is compressed to about 28 atm. and desulphurized using the Rectisol process. The subsequent process steps are similar to that described for the partial oxidation of furnace oil. A typical process block diagram is shown in Fig. 3. Except

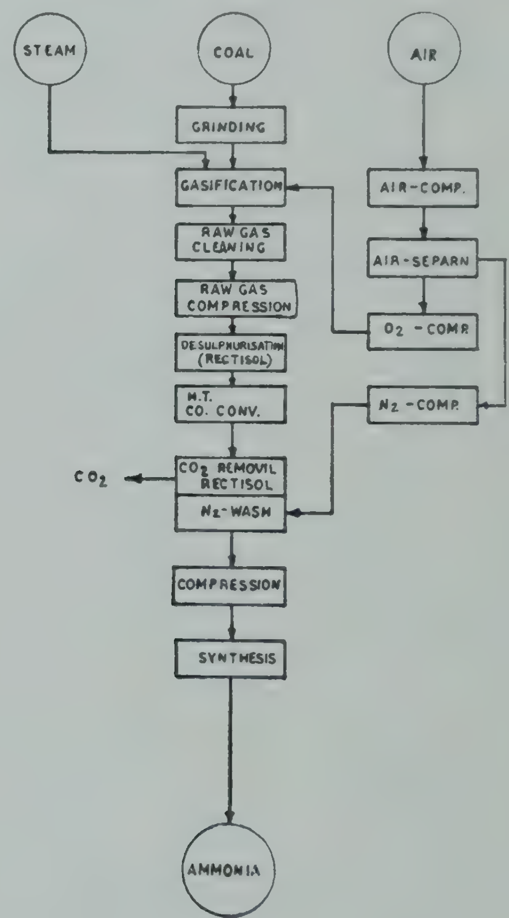

Fig. 3—Coal Based Ammonia Plant

for the gasifiers, the plants are to be in single stream, using centrifugal compressors. The capacity is 900 te ammonia/day.

Compared to the partial oxidation of furnace oil under pressure, the main differences are: (i) the provision of coal handling and grinding facilities; (ii) gasifier operation at atmospheric pressure; (iii) elaborate raw gas cleaning facilities including an electrostatic precipitator; and (iv) raw gas compression from about atmospheric pressure to the gas purification pressure.

TABLE 4—FEEDSTOCKS REQUIREMENT WITH THEIR COSTS IN 1971 AND 1975

Plant	Feedstock	Feedstock requirement Kcal/te $NH_3 \times 10^6$	Cost in 1971		Probable Cost in 1975	
			Rs./10^6 Kcal	Rs./te NH_3	Rs.10^6 Kcal	Rs./te NH_3
A	Natural Gas	9.95	15.1	150	22.6	225
B	Naphtha (Reciprocating)	8.50	20.4[5]	173	27.4	232
C	Naphtha (Centrifugal)	10.45	15.6	163	21.9	229
D	Heavy Stocks	8.20	13.4	110	18.8	152
E	Coal	11.10	6.9	77	8.6	95

[5] Includes pipeline transport cost.

Requirements of Feedstocks, Utilities, Investment Costs, Production Costs, etc. for Ammonia Plants Using Various Feedstocks

The typical ammonia plants that are being subjected to analysis in the following paragraphs form part of fertilizer complexes; the end-products are either urea alone, or urea and NPK products. Five typical plants have been taken for an analytical study.

Plant A: The plant is located inland near natural gas fields and natural gas is the feedstock. The plant capacity is 910 tonnes per day in single stream using centrifugal compressors. The process scheme is similar to that in Fig. 1. The plant is expected to be commissioned in mid-1974.

Plant B: An inland location and the feedstock naphtha is piped to the plant, which is in two streams using reciprocating compressors and is based on steam-naphtha reforming process. The process scheme is similar to that in Fig. 1. The capacity is 830 te/d ammonia. The plant is in operation for about one year.

Plant C: It is a coastal location and is based on steam-naphtha reformation. The plant uses centrifugal compressors and is in single stream. The process scheme is similar to Fig. 1. The capacity of the plant is 660 te/d ammonia. The plant is expected to be commissioned in mid-1973.

Plant D: This plant using partial oxidation of heavy stock has a coastal location. It uses the single stream concept except for the gasifiers, which are in multiple units. Centrifugal compressors are used for all services. Fig. 2 gives the process scheme. The capacity of the plant is 600 te/d ammonia. The plant is expected to be commissioned in 1975.

Plant E: Using suspension gasification of powdered coal with oxygen this plant is located inland practically on the coal mine. The plant is in single stream except for the multiple gasifiers. Gas air compression is done in centrifugal compressors. The plant capacity is 900 te/d ammonia. Fig. 3 gives the process scheme. The plant is expected to be commissioned in mid-1975.

The feedstock requirement for the plants illustrated above in terms of their heat value, along with their cost in 1971 and their probable cost in 1975, is shown in Table 4.

The costs for petroleum-based feedstocks have been computed on the basis of the price of the crude oil at \$ 1.28 per barrel prevailing in January 1971. Recently, there had been an increase in the price of crude and it has generally been agreed that the same is to go up further. The feedstock costs in 1975 include an estimated increase due to the rise in the crude price to \$ 2.05 by 1975. For coal, the cost at Rs. 38.7 per tonne in 1971 has been assumed at Rs. 50/te in 1975. The cost for coal as feedstock is the lowest followed by that of heavy stocks. The cost of utilities and fuel for the various plants is given in Table 5.

The investment costs for the ammonia plant alone and ammonia plant with the auxiliary facilities (proportionate

TABLE 5—COST OF UTILITIES AND FUEL

Utilities	Plants				
	A	B	C	D	E
1. Power, Rs./MWH	120.0	49.4	95.0	85.0	52.0
2. Water, Rs./M^3	0.12	0.03	0.3	***	0.01
3. Coal, Rs./te	—	—	—	55.0	38.7

***Water will be obtained from tubewell located within the factory

costs), contingency, financing charges, pre-operating expenses, etc. are given in Table 6, for various plants.

The columns 1 and 4 (Table 6) give the figures as calculated from the respective project estimates. However, as these estimates have been made at different times and under different credit systems and fiscal policies they are not strictly comparable. An attempt has been made to bring these figures on a common basis as far as time and fiscal policies are concerned. The adjusted figures are given in columns 2, 3, 5 and 6.

TABLE 6—INVESTMENT COSTS FOR AMMONIA PLANT AND THE SAME PLANT WITH AUXILIARY FACILITIES

Plant	Investment/Annual Tonne of Ammonia					
	Battery Limits Plant Costs			Total including Facilities and Financing Charges		
	According to Project Estimate	Common Basis Rs.	Common Basis R. I[1]	According to Project Estimate	Common Basis Rs.	Common Basis R.I[1]
1	2	3	4	5	6	7
A	702	702	100	985	985	100
B	649	810	115	842	1052	107
C	812	910	130	1106	1240	124
D	1172	1120	160	1738	1520	154
E	1656	1585	226	2050	1979	201

[1] Relative indices

The plant A, based on natural gas, has the lowest investment; others follow expected pattern depending upon feedstock and plant size. However, as the design and supply of equipment are from different countries and organizations and strictly not on competitive basis, these figures are not strictly comparable. But they do provide a broad yardstick for evaluation.

The plant D, based on partial oxidation of heavy stocks, requires about 24 per cent more investment than the comparable plant C based on steam-naphtha reformation. The reasons are mainly due to the requirement of a large air and a large steam generation plants. In addition, more processing steps, like desulphurization of raw gas, are also involved.

The plant E, based on powdered coal gasification with oxygen requires the maximum investment. The investment required for coal-based plant works out to about 88 per cent more than a comparably sized plant based on steam-naphtha reforming and about 30 per cent more than a comparable plant based on partial oxidation of heavy residues. The reasons for the increased investment are (i) larger sized air and steam generation plants are required in a coal-based plant than in a plant based on partial oxidation of heavy stock and (ii) coal handling/preparation facilities required. Since the gasification of coal takes place at atmospheric pressure, in addition to low pressure gas cleaning equipment, raw gas compression facilities are also required. Large capacity plants, like plant E, based on single stream concept, are so far not in operation. But there had been a number of plants based on the powdered gas coal gasification of smaller capacity.

The estimated cost of production of ammonia, with the 1971 and 1975 feedstock prices, are shown in Table 7 for the plants A, B, C, D and E. The relative indices for the cost of feedstocks and costs of production of ammonia before and after depreciation and interest are shown in Table 8.

As discussed earlier, the cost of feedstock alone is the lowest for the coal-based plant E, followed by heavy stock based plant D and the natural gas based plant A. The situation is more favourable for the coal-based plant with the probable feedstock price in 1975 as the cost of naphtha is likely to go up by that time. It has been estimated that the price rise of naphtha would be proportional to the rise in crude price. In fact, the worldwide demand for naphtha for petrochemicals is likely to further harden the naphtha price in international trade. The developing countries of Asia, Africa and Latin America are likely to be the worst sufferers as far as naphtha supply for ammonia production is concerned.

The cost of production of ammonia before depreciation and interest is more or less same for the feedstocks naphtha, heavy stocks and coal in 1971 but is likely to be lower by about 8 per cent in 1975 in the case of heavy stocks and coal-based plants compared to that for naphtha-based ammonia.

The cost of production of ammonia after depreciation and interest is marginally by 5 per cent in the case of heavy stocks based plant and for plant B and by 21 per cent in the case of coal based plant with 1971 feedstock prices. With the 1975 feedstock prices, the ammonia production cost based on heavy stocks is expected to remain about the same and that based on coal might be 10 per cent higher than that based on naphtha. The major reason for the competitiveness of heavy stocks and coal in 1975 is that the effect of higher investment for these plants is neutralized by the likely higher price of naphtha.

TABLE 7—COST OF PRODUCTION FOR TYPICAL AMMONIA PLANTS (A, B, C, D & E)

Cost Element		PLANTS				
		A	B	C	D	E
		Rs./ tonne ammonia				
1. Feedstock	—1971	150	173	163	110	77
"	—1975	225	223	230	152	99
2. Utilities	—1971	9	38	14	46	71
"	—1975	9	38	14	53	80
3. Consumables and Maintenance Materials		45	79	51	57	76
4. Labour and Overheads		10	11	11	11	13
5. Insurance, Local taxes, general expenses, interest on working capital and contingency		20	27	20	25	30
6. Credit for steam		—	34	—	—	—
7. Cost of production before depreciation and interest	—1971	234	294	259	249	267
	—1975	309	344	326	298	298
8. Depreciation		99	105	124	152	198
9. Cost of production after adjusting depreciation and interest	—1971	333	399	383	401	465
	—1975	408	449	450	450	496

TABLE 8—RELATIVE INDICES FOR COST OF FEEDSTOCKS AND COST OF PRODUCTION FOR VARIOUS AMMONIA PLANTS

		Plants				
		A	B	C	D	E
		Natural Gas	Naphtha Recipro-cating	Naphtha Centri-fugal	Heavy Stock	Coal
1. Feedstock	—1971	92	106	100	67	47
	—1975	98	97	100	66	43
2. Cost of Production (*i*) Before depreciation and interest	—1971	90	113	100	96	103
	—1975	95	105	100	92	92
(*ii*) After depreciation and interest	—1971	87	105	100	105	121
	—1975	91	100	100	100	110

Feedstocks for Future Ammonia Plants

Petroleum Crude: A scheme has been studied to utilize 1.25 million tonnes of crude per year for the production of one million tonnes of fertilizers nitrogen by subjecting the crude to a simple distillation step in a topping unit so that the distillation products would provide feedstock for 4,600 tonnes/day of ammonia as below: (i) feedstock naphtha requirements of a 600 te/d ammonia plant based on steam reformation; (ii) feed naphtha and fuel (light distillates) requirements of a 1000 te/d ammonia plant based on steam reformation; and (iii) residual heavy stock requirements of three 1000 te/d ammonia plants based on partial oxidation.

The economics of the crude topping unit and the associated ammonia plants appear attractive and would be preferable to the use of crude as such, as a feedstock in all the four ammonia plants. Such one million tonne nitrogen production facility from a group of four units could be duplicated to attain the targeted requirements for nitrogenous fertilizers.

Heavy Stocks: Heavy stocks are available at about the same price as crude oil (weight basis) and their import —if not available indigenously—could be considered for the production of ammonia. Specially for inland locations, transport of fuel oil would be cheaper than that of naphtha.

Coal: Suitable coal is available indigenously in adequate quantities in several specific locations. An essential pre-requisite for the success of a coal-based plant would be a thorough investigation to ensure that not only the supplies of coal would be available from the mines for a specified number of years, but the quality of coal including the ash content and ash characteristics, must not widely vary during the useful period of plant life. Thorough investigations, therefore, are called for, inclusive of extensive borehole tests over wide areas before investment decisions for a coal-based plant could be considered. It is necessary to emphasize that mere abundant availability of coal from a number of sources of varying quality would not necessarily contribute to the success of a coal-based plant.

Normally, coal-based plants should be situated near the mine-head to avoid bottlenecks and double handling of coal. Minimum rehandling of coal will lead to a smoother operation. Further transport and handling costs must be kept to the minimum. Under such circumstances, developing countries would do well to consider coal as a suitable alternative for ammonia production. It should, however, be recognized that on-stream time of coal-based plants might be lower as the maintenance requirements are heavy. Therefore, adequate provision for spare equipment is essential, and this would contribute to higher capital investment. The sections relating to gas cleaning should be adequately designed in order that the dust content could be brought down to a negligible value to provide reasonable trouble-free operation of the compressors.

Foreign Exchange Requirement for Feedstocks

This analysis is restricted to the following feedstocks, viz. coal, naphtha, heavy stocks and crude, as these are the likely raw materials on which the future production of ammonia in India would be based. Indigenous naphtha would not be available after meeting the requirements of the naphtha-based plants, and, therefore, if any future ammonia capacity is to be based on naphtha, it would require import of naphtha. Heavy stocks and crude petroleum might be obtained both from indigenous and imported sources.

The annual foreign exchange outgo would comprise of (a) importing the feedstock (b) servicing of foreign exchange capital and loan; and (c) buying spares and catalysts requiring import. Table 9 shows the foreign exchange requirement for feedstock and servicing of foreign exchange capital and loan along with the requirement for spares and catalysts requiring import. In computing the servicing of foreign exchange capital and loan, it has been assumed that the repayment would be effected in ten equal annual instalments after an initial period of three years. Interest has been computed at 8 per cent per year from the dates of drawal. The total foreign exchange outgo over the ten-year period for repayment of capital inclusive of interest and for yearly purchases of feedstocks and imports of spares, catalysts and chemicals has been computed for six different alternatives (Table 9). The total production of ammonia during the ten-year period has been estimated and the foreign exchange outgo per tonne of ammonia has been computed on this basis:

TABLE 9—FOREIGN EXCHANGE OUTGO, RS./TE AMMONIA

Feedstock	Feedstock Cost in 1975, Rs.	Capital, Interest Repayment, Spares & Catalysts Rs.	Total
1. Crude (Indigenous)	—	120	120
2. Heavy Stock (Indigenous)	—	115	115
3. Coal (Indigenous)	—	128	128
4. Crude (Imported)	93	120	213
5. Heavy Stock (Imported)	92	115	207
6. Naphtha (Imported)	230	133	363

The foreign exchange requirement for the production of ammonia is lowest in the case of indigenous feedstocks. The petroleum feedstocks-based ammonia requires lesser amount of foreign exchange than the coal-based one. The foreign exchange requirement is the highest in the case of imported naphtha-based ammonia; for imported heavy stock-based ammonia it is about same as that of the imported crude-based one.

The current position in India in respect of choice of feedstocks in the expanding nitrogen fertilizer industry is somewhat complicated. It has been shown earlier that of the 5.6 million tonnes of ammonia capacity, about 50 per cent is already based on naphtha. This programme itself would call for import of substantial quantities of naphtha, probably at least of the order of 1 to 1.5 million tonnes by 1975 or so. India's nitrogen requirement by 1985 would call for nearly doubling the ammonia capacity that has already been approved for construction. The question of further imports of naphtha or petroleum feedstocks for the new capacity that has to be installed between 1975-85 would have to be viewed in this context.

Until now, the crude reserves have proved inadequate

to meet the demand of petroleum feedstocks. Until more crude oil reserves are, therefore, proved, it would be risky to continue to depend on petroleum feedstocks for our expanding nitrogen programme from a long-term point of view. The position in this respect, however, is far from clear. There are some indications of large reserves of crude oil being found off-shore on the Gujarat coast. It is, therefore, possible that the off-shore crude may provide enough not merely to meet India's petroleum demands, but also some surplus to meet at least a part of the nitrogen demands. If that happens, the adoption of coal technology for nitrogen programme in a big way would no longer be required.

However, in the event of the expectations of off-shore crude proving disappointing, the coal based projects would provide adequate experience and data for further consideration of expansion of the industry based on coal for the 1978-79 programme and beyond.

Research Note

The mixed fluor-chlorapatites of lead have been prepared from aqueous solutions.

Preparation and Cell Dimensions of Mixed Fluor-Chlorapatites of Lead

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A number of synthetic compounds, isomorphous with apatite, can be prepared in which chlorine and fluorine are mutually substituted. They are often described as mixed apatites. Apparently one fluorine atom replaces or substitutes one chlorine atom and *vice versa* but products containing different amounts of fluorine and chlorine have been reported[1,2].

The mixed calcium apatites have been prepared[1] by heating together calculated quantities of β-$Ca_3(PO_4)_2$, calcium chloride and calcium fluoride at 800°C. or by treating a pure synthetic chlorapatite with different amounts of calcium fluoride. The unit cell dimensions of calcium fluorapatite and calcium chlorapatite are as follows[3]:

$Ca_{10}(PO_4)_6F_2$	a=9.36 Å	c=6.88 Å	c/a=0.735
$Ca_{10}(PO_4)_6Cl_2$	a=9.63 Å	c=6.78 Å	c/a=0.704

The unit cell dimensions of a mixed fluor-chlorapatite given by Wallaeys[1] are: a=9.45 Å, c=6.84 Å and c/a = 0.723. Hentschel[4] carried out x-ray measurements upon a mixed fluor-chlorapatite from Jumilla, (Spain) containing about 0.6 per cent chlorine and gave a=9.41 Å, c=6.88 Å and c/a = 0.731. Mehmel[5] also studied a mixed apatite from Jumilla, containing 0.47 per cent chlorine and 3.54 per cent fluorine. He reported the following unit cell dimensions: a=9.36 Å, c=6.85 Å and c/a = 0.731. The dimensions of the unit of structure containing $Ca_{10}(Cl.X)_2(PO_4)_6$ where X was possibly oxygen or hydroxyl have been given by Hendricks *et al*[6] as: a = 9.52Å, c=6.85Å and c/a=0.719. The cell constants of a number of synthetic mixed fluor-chloıapatites of calcium have been given by Bhatnagar[2].

It is possible that a compound, lead fluor-chlorapatite of probable composition, $Pb_{10}(PO_4)_6(F, Cl)_2$, can be considered as existing with an ordered arrangement of the fluorine and chlorine atoms. Since the radius of the F^- ion (1.36 Å) is very close to that of the Cl^- ion (1.81 Å), both groups may replace or substitute each other without appreciable alternation in the structure. The x-ray diffraction patterns will be similar to apatites.

This is perhaps the first investigation on the preparation of mixed fluor-chlorapatites of lead. The two preparations were attempted as follows:

1. The lead solutions, lead acetate (2.56 g./200 ml.), lead chloride (0.5 g./200 ml.) and lead fluoride (0.5 g./200 ml.), were mixed together and heated at about 100°C. for 20 minutes. The disodium hydrogen phosphate solution (5.76 g./200 ml.) was added dropwise to this mixed solution at 100°C. The whole system was continuously stirred for about 22 hours, filtered, washed with distilled water and dried at 100°C. The unit cell dimensions are: a=9.96 Å, c=7.35 Å and c/a=0.737.

2. Ammonium chloride (0.27 g./100 ml.) and ammonium fluoride (0.19 g./100 ml.) were mixed together. Then this solution and a solution of diammonium hydrogen phosphate (3.96 g./300 ml.) were taken in separate containers and added dropwise with stirring to lead acetate solution (16.26 g./300 ml.) at 100°C. The reacting mixture was stirred for about 24 hours, filtered, washed with distilled water and dried at 100°C. The cell constants of this product are: a=9.92 Å, c=7.34 Å and c/a=0.739. It seems that the unit cell dimensions and composition of mixed apatites of lead are dependent on the preparation

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process. The unit cell dimensions of synthetic lead fluorapatite and lead chlorapatite are given below for comparison with the mixed fluor-chlorapatite of lead.

$Pb_{10}(PO_4)_6F_2$	a=9.78 Å	c=7.30 Å	c/a=0.746
$Pb_{10}(PO_4)_6Cl_2$	a=9.99 Å	c=7.34 Å	c/a=0.734

Acknowledgement

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Technical Digest

Coke Level Indicator

Planning & Development Division of Fertilizer Corporation of India has developed a Coke Level Indicator from indigenous components. It is a versatile transistorized instrument using Cobalt-60 radioactive source and a thin-walled Geiger-Muller tube as detector. The model 710001 of the indicator has been specially designed for monitoring the level of coke in a bunker of a Lean Gas Producer having a diameter of about four meters inside which the width of the coke bed at the critical level is about one metre. The moment coke level drops below the critical position, the indicator accentuates an external audible or visual alarm or both, operated by an electromagnetic relay. The instrument, with suitable modifications, can be used for monitoring all types of solid or liquid levels, such as in hot vessels, closed charging bunkers, solid fuel furnaces, evaporators, tankers for liquefied process chemicals, loops for liquid by-pass, safety vents and many other situations in the chemical/metallurgical industry. These can be made almost totally independent of many troubling parameters that normally interfere with precision instrumentation, such as corrosion, explosion hazards, turbulence, frothing, fluid's coarseness, entrapped voids, temperature/pressure considerations, chemical reactivity, etc. The instrument is tailor-made to suit each application.

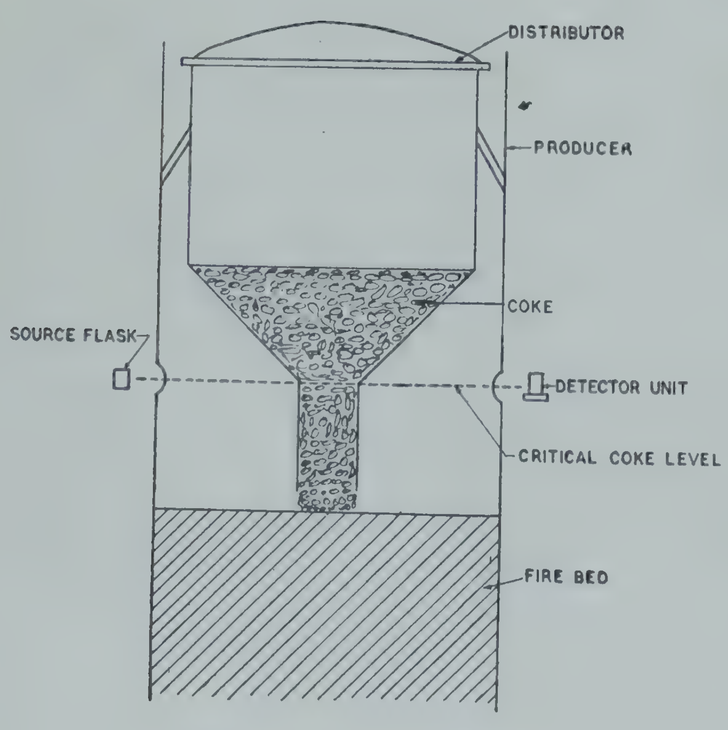

Fig. 1—Coke Level Indicator

The **source flask** weighing about 750 kg. has been designed to hold a 250 millicurie Cobalt-60 source of half life 5.3 years. The outer casing is made up of mild steel and is filled with lead for shielding. The moving parts and the collimating arrangements are fabricated from stainless steel. The source is located within a collimating cylinder assembly, which in the 'Radiation On' position, delivers a fine pencil cone of gamma-rays with semi angle of about 2°. The **detector unit** consists of a G.M. tube of thin-walled halogen quenched type, operating at 400 V, d.c. A transistorized pre-amplifier of low gain is

Fig. 2—Detector Assembly

built-in within the detector unit and the assembly is enclosed in a double walled brass jacket for circulation of cooling water to protect it from ambient temperature which may be around 40° to 60°C. The **control box** accommodates the entire circuit beyond the pre-amplifier stage, and is designed to withstand sufficient noise level, dust nuisance and continued operation requirements for industrial installations.

Instrument for Instantaneous and Non-destructive Estimation of Ferrite in Stainless Steel.

For instantaneous and non-destructive estimation of ferrite in austenitic stainless steels, a portable instrument suitable for field application has been designed and developed by the Physical Research Wing of the Planning and Development Division, FCI Ltd., Sindri. Its battery-operated transistorized circuit was built from entirely indigeneous components. Faulty welding techniques result in build-up of large concentrations of ferrite in stainless steel welds and during plant operation these parts are susceptible to corrosion. The instrument developed will be particularly useful in testing of welds during fabrication of plant equipments before their installation. Testing with this instrument will result in considerable savings in reducing replacement costs and downtime losses.

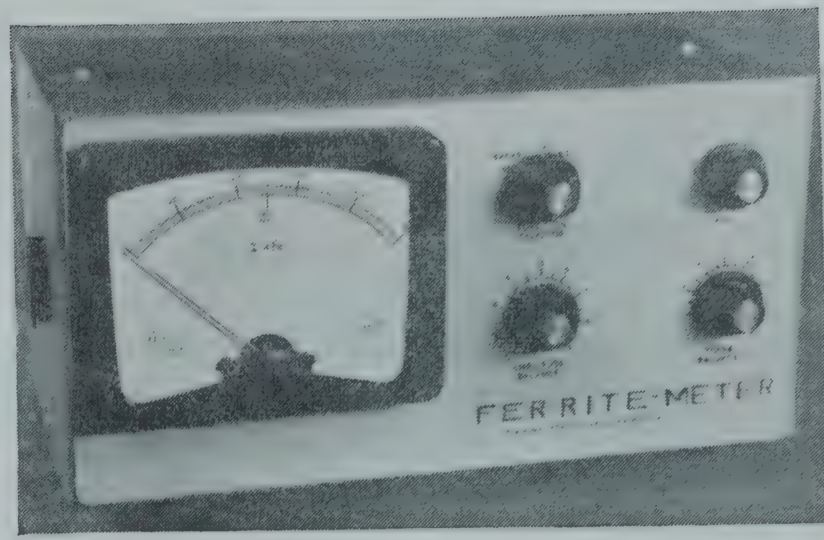

Fig. 3—Ferritemeter for Determining Ferrite in Stainless Steel Developed by P and D Division, FCI Ltd.

Seminars & Conferences

Seminar on Coordinated Marketing and Use of Fertilizers and Other Inputs

This seminar organized by the Fertilizer Association of India at New Delhi on December 10-12, 1971 discussed various facets of the coordinated approach towards use and marketing of fertilizers, water management in relation to efficient use of fertilizers, financing for optimum use of fertilizers, mechanisation in the use of fertilizers, use of improved seeds in relation to efficient use of fertilizers, use of plant protection chemicals and integrated promotion and marketing of agricultural inputs. There is the expectation that given a proper policy framework, the gains obtained by the use of high yield variety seeds and modern agricultural inputs could be consolidated and agricultural prosperity sustained. There has been a rapid transformation of the sellers' market of fertilizers into a buyers' one. The total consumption of all types of fertilizers taken together in 1969-70, in terms of nutrients, is estimated at 2.011 million tonnes as against 0.755 million tonnes in 1965-66, 0.306 million tonnes in 1960-61 and only 69,000 tonnes in 1950-51. The consumption of nitrogen has increased 10 times, that of phosphoric acid by 15 times and that of potash by 13 times in last ten years. But in spite of the impressive growth in fertilizer consumption during these years there is vast majority of small and common farmers who because of their low purchasing capacity and small investment propensities cannot afford to use high priced fertilizers even in modest doses. They would not make more expenditure involving greater risk.

Another reason for low consumption of fertilizers, and adoption of high yield variety seeds in agriculture along with other modern scientific inputs of the poor farmers may be their backwardness and prejudice to change to new techniques, So the aim of marketing should be such that the benefits of modern technology of agriculture could be shared by farmers belonging to all strata.

The fourth five year plan aims at an output of 129 million tonnes of foodgrains, 10.50 tonnes of oil seeds, 1.50 million tonnes of sugarcane, 8.00 million bales of cotton and 7.40 million bales of jute besides envisaging a substantial increase in production of other agricultural crops. Achievement of these targets requires a three-fold increase in the consumption of fertilizers i.e. 5.50 million tonnes in 1973-74 consisting of 3.20 million tonnes of nitrogen, 1.40 million tonnes of phosphate and 0.90 million tonnes of potash, from a level of 1.76 million tonnes of nutrients in 1968-69. Another problem facing Indian agriculture is the lack of balanced fertilization. While in paddy-growing countries like Japan the ratio of N, P and K use has been 1:1:1, India is aiming at a ratio of 4:2:1 by 1973-74. The actual ratio in 1968-69 was 8:2.6:1 and much leeway is yet to be made to meet the balance aimed at in the fourth plan. One hundred centres are proposed to be set up in the intensive districts in a phased manner during the fourth plan for organizing training and education of farmers in the balanced use of fertilizers. Some enlightened manufacturers have expanded their promotional services including field demonstrations and audio-visual publicity. This has to grow into a general movement. Soil testing laboratories have been set up in the states and mobile soil testing vans are also being introduced in the field. Enterprising young men who have requisite training in the concerned disciplines should set up private practice in soil testing. They will be able to penetrate into the rural interior and bring the service right upto the doorsteps of the farmer.

Credit is the most important of the inputs. The short term and medium term advances of agricultural credit societies are expected to increase from Rs. 3,930 millions and Rs. 350 millions in 1967-68 to Rs. 6,900 and Rs. 900 millions in 1973-74. It is proposed that in future agricultural credit will be dispersed not only by the cooperatives but also by the commercial banks, agro-industries corporations and other institutions. It is expected that by the end of fourth plan 25 million hectares, would be cultivated with the high yield varieties of seeds.

With the nationalization of banks, the extension of facilities of loan to hitherto unbanked areas is proceeding satisfactorily.

Water is a basic input, especially in the context of high yielding varieties and increased fertilizer application. In between 1965-66 and 1969-70 the number of pump sets for lift irrigation has more than doubled, reaching a level of 2.1 millions and the number of private

tube wells has increased to the level of 0.38 million. In the fourth plan period the total investment in ground water development will be of Rs. 16,500 millions. More attention will have to be given to scientific and systematic tapping of this ground water. The National Seeds Corporation and the Central and State Farms are now able to meet the demand for seeds fairly satisfactorily. For efficient farming use of pesticides is essential. The present indigeneous production of pesticides is expected to be sufficient to cover 80 million hectares under plant protection measures.

Dr. Swaminathan, Director IARI, discussed on synergistic effects of coordinated use of fertilizers and other inputs. Package of practices, comprising the use of seeds, high-yielding hybrid varieties with adequate and timely supply of plant nutrients through fertilizers and water followed by adoption of suitable agronomic technology and prophylactic measures as well as post-harvest technology of storage, processing, etc. is the pivot on which new strategy of agriculture is based. The release of synergistic interactions provides the best possible means of enhancing the cost-benefit ratio of developmental strategies. Dr. Swaminathan described a few examples of the types of interactions between fertilizer use of other inputs. While the research worker usually recommends a production-maximizing dose, a farmer tends to choose a profit-maximizing dose of fertilizer. These two doses are different.

The farmer for adopting modern inputs requires not only training but also credit at the time of sowing. Dr. Dastane, Special Officer-Irrigation, IARI, summarizing the points raised in the papers on water management in relation to efficient use of fertilizers said that 45 per cent of the total available water resources were being used to irrigate rice crop alone and it was estimated that two-thirds of the irrigation water applied to this crop was lost by percolation. Considerable loss of nutrients particularly nitrate nitrogen, was taking place along with the percolation. Dr. Dastane felt that if slow releasing nitrogenous fertilizers similar to oil cakes were manufactured and used, nitrogen loss could be minimized. A coating of urea with neem cake and coal-tar had shown some promise in recent studies and had helped in saving nitrogen losses to the tune of 50 per cent.

Adequate data on water requirement of most of the crops and their responses to fertilizers had already been collected. The Agronomy Division of Indian Agricultural Research Institute had compiled the available information and could supply it to interested persons.

Dr. Dastane pointed out that at present 60 million acres (24 million hectares) were covered by irrigated cereal and pulse crops in the country. If all the other inputs were made available and used in time, 2 tonnes of foodgrains could be easily produced per acre (5 tonnes per hectare). Thus, 120 million tonnes of foodgrains, which would approximately be our need by 1973-74, could be obtained only from these 60 million acres. If proper practices were adopted in the rainfed areas, we would not face any food problem for the next 25 years. He was confident that all this was possible of achievement within the available resources and could be done without any extra cost. Proper planning and coordination of all the production programmes are, however, essential to realise this potential.

Commenting on the general belief that application of fertilizers increased the water requirement of crops, Dr. Dastane said that this was not true. Water requirement of crop plants was primarily governed by weather factors and energy required for *evapotranspiration*. Hardly 0.1 per cent of the total water taken up by plants from the soil was retained in their system. On the contrary, application of fertilizers increased the efficiency of water by enabling production of higher dry matter per unit of water than that obtained in the absence of fertilizers.

In the discussion that followed, considerable emphasis was laid on the dissemination of available research data among farmers. It was feared that unless an intelligent action programme was taken up in the country with regard to combined use of water and fertilizers, full advantages from the established practices would not be realised. If the farmers were expected to adopt appropriate water management practices for their crops, they must be supplied with such of the information as was available on scheduling of irrigations, total quantity of water to be applied per crop season, etc.

The necessity of undertaking per irrigation soil surveys was brought out by some of the participants. This was particularly essential to determine the type of drainage system required in a given area. Crop lands coming under multiple cropping would receive huge quantity of water in one year. Pre-irrigation soil survey would be of considerable help under such conditions particularly in case of black soils.

The question of charges for water supplied to farmers was discussed at length. It was felt that the present charges in India were perhaps the lowest in the world. Farmers were not using properly the water supplied to them because they were not spending much on this item. Considerable variation in charges existed from project to project not only in different states but also within a State. It was essential to adopt uniform policy throughout the country. Irrigation Commission of the Government

of India was studying this matter. A view was expressed that the farmers could be charged about 6 to 10 per cent of the extra income which they would obtain through irrigation.

With reference to the water management cooperatives as they exist in the USA, it was thought that attempts should be made to formulate groups of farmers so that they could take up distribution of water themselves on a cooperative basis. This practice was being adopted to some extent in parts of Maharashtra.

Referring to the rainfed areas, the participants felt that more research should be undertaken to bring out the beneficial role played by fertilizers in increasing crop yields. Package of practices should be clearly enunciated for crops grown in different low rainfall regions so that farmers could get precise instructions.

The need for conducting hydrological surveys particularly in areas where loans for digging wells were being advanced freely was expressed by some of the participants. Greater combined use of ground and canal water sources was found desirable.

In his concluding remakrs, Dr. Krantz said that several speakers had highlighted the problems of water management in monsoon season including the problems of drainage. Greater use of canal and ground water sources was advocated. Since water management probelms of a localized nature were commonly observed, it was necessary to employ trained people in each area who could evolve appropriate solutions and guide the farmers.

After the presentation of papers on financing for optimum use of fertilizers, the chairman made observations on the credit needs of farmers and fertilizer dealers. The following points were touched upon in course of the discussion: (1) the agriculture-based industry should be encouraged to take up credit distribution; (2) farmers would take to the use of fertilizers, improved seeds etc. if there was an adequate price guarantee. Credit was only a minor problem when compared to the problem of guaranteed price; and (3) selected fertilizer dealers should be encouraged to provide loans to small farmers for purchase of fertilizers.

A comparison of the effects of credit and subsidy schemes on the use of fertilizers was made by D. N. Truscott and K. Bose of Humphreys and Glasgow Ltd., Bombay. Credit and subsidy schemes both have their places in encouraging the use of fertilizers to improve crop yields, credit schemes have to be confined to the larger farms because the administration costs rise with the credit holders and the risks rapidly for small farms. A subsidy scheme increases the crops of the farms below, at and just above the subsistence level. There is a considerable proportion of the total cultivated area of a country in such farms. A subsidy scheme, in addition to its effects on the crop of larger farms, is likely to make a major improvement in the total crop yield of a country as compared to a credit scheme. Actual quantum of fertilizers used will depend on a number of factors that might come into play independently and though credit is a necessary help for enabling farmers to procure fertilizers and other inputs, availability of credit alone is not decisive in bringing about actual use of fertilizers and other inputs. Because the demand for certain fertilizers may undergo erratic shifts in an agriculture season. Purchase of fertilizer in rainfed agriculture depends on timely and adequate rainfall, where there is no good rainfail demand of fertilizers will be less and if there is good rainfall the demand will be more than supply. This results in the imbalances in marketing of fertilizers.

Some recommendations were made on the credit system to increase the availability of credit to the farmer. For increasing production crop insurance should be introduced as it would help financing institutions to provide adequate credit to the farmer. Credit facilities for longer periods were important for the distribution system to extend to interior areas. undeveloped areas, single cropped areas etc. The present pool system of fertilizers could take into account this aspect and provide such a facility to distributors as well as cooperatives in order that they might take the fertilizer to the interior areas to help in increasing production. The experiences in the past had revealed that dealers should not be given credit facilities to extend in turn credit to farmers. Adequate rapport should be reached between the distributors and the banks for ensuring the necessary credit flow.

The role of machines in relation to efficient use of fertilizers was pointed out in several papers. In the present context of our developing agricultural economy the role of mechanization is a controversial one. The short term effect of the introduction of some machines is to replace one or several men, however, the long term effect is increased productivity. Dr. A. M. Michael, Senior Research Engineer, Division of Agricultural Engineering IARI, referred to the following points brought out by different authors in their papers: (1) Mechanization would not replace labour but would rather enhance its efficiency; (2) while the use of a fertilizer drill increased the yield by 40 per cent, the increase was not so spectacular as to permit purchase of a drill costing about 700 rupees by all the farmers, There was, therefore, a need for custom or hire service in case of this and other equipment; and (3) it was not proper to drop fertilizers

and seeds through the same spout. Trials at IARI had shown that placement of fertilizers and seeds at different levels was not necessary in irrigated areas. However, in rainfed areas placement of fertilizers at deeper levels than seeds was called for.

Dr. Michael referred to the development of seed-cum-fertilizer drills by the Indian Council of Agricultural Research (ICAR) and indicated that the drills presently available were mostly of the type which put seed and fertilizer through separate spouts. He also stated that the ICAR were actively engaged in the development of anhydrous ammonia applicator which would suit the farming conditions in India.

In the discussions that followed, several delegates pointed out that though a number of seed fertilizer drills had been developed by research stations or introduced by the industry, these had not adequately met the needs of the farmer. It was felt that designs of such machines as were found suitable should be finalised and that they should be manufactured in sufficient numbers and in different sizes to reach the farmer.

Several delegates pointed out that if the benefits of modern technology were to reach the small farmer, there was an urgent need for having a well organized set-up for customers' service for tractors and tractor-drawn as well as animal-drawn equipment. It was felt by some speakers that in view of the fact that the sizes of farm holdings were getting reduced, the possibilities of manufacture and use of two wheel tractors (tillers) should be explored. The need for developing paddy transplanters and cotton pickers to suit Indian conditions was stressed by several speakers.

Considerable interest was shown by delegates on the possibility of using anhydrous ammonia, nitrogen solutions and fluid fertilizers under Indian conditions. In the course of discussions, several questions were raised regarding the comparative efficiencies of solid and fluid fertilizers, the types of equipment necessary for their application, the soil and climatic conditions under which ammonia could be used, etc. While answering these questions based on U.S. experience, Mr. J. L. Strauss pointed out that application of anhydrous ammonia was not generally recommended in sandy soils and of such application was necessary the applicator should have more tines. He also referred to the need for application of anhydrous ammonia in dry rather than wet soil to reduce volatilisation losses. In view of the high clay content and consequent difficulty in working, use of ammonia applicators in black soil might be relatively difficult.

Several delegates stressed the need for the development of a bullock-drawn ammonia applicator in the country. It was also pointed out that a network of agencies would have to be set up to distribute ammonia in suitable containers.

Use of improved seeds which has an important role in bringing green revolution in the country was discussed by various participants of the seminar. The yield potential of seeds of high-yielding varieties cannot be fully realized unless the other agricultural imputs, such as fertilizers, pesticides, etc., are used in the right quantities. Improved varieties of seeds require extra sophistication and therefore massive extension education programmes are called for. Meaningful demonstrations should be carried out in an extensive scale to show the beneficial effects. The need for evolving better varieties of seeds adapted to different agro-climatic conditions with high-yielding disease and drought-resistant characteristics and of acceptable grain type was stressed by several speakers.

With the introduction of new high yield varieties of crops for growing in irrigated areas under high fertility conditions the probability of insect pests and plant diseases developing rapidly into epidemic proportions has increased several fold. A number of papers on pest control and plant protection chemicals were read. In India after the introduction of high yielding varieties the use of fertilizer has increased 5 times from 1964-65 to 1967-68 but that of pesticides about 2 times only. Dr. S. N. Banerjee, Plant Protection Adviser, Directorate of Plant Protection, Quarantine and Storage, New Delhi, said that for every kilogram of fertilizer, Japan uses 36 g. of pesticides, U.S.A. about 96 g. and in Europe it is about 20 g. Not only per kilogram of fertilizer but also per acreage consumption of pesticide is very low in India. The crop losses in India due to insects, pests, etc. are estimated to be around Rs. 10,000 millions .The losses varied from State to State. The losses are as high as 40 per cent in cotton and as low 3 per cent in wheat. For the other crops, the estimated losses range from 9 to 15 per cent. The Indian pesticides Industry is currently manufacturing 39 basic pesticidal chemicals and due to poor demand only 50 per cent of the installed capacity is being utilized. Different equipments for use of pesticides were duscussed. Hazards in the application of pesticides were also discussed. Combined aerial application of pesticides and fertilizers has shown great promise in dry farming as well as irrigated areas.

Integrated promotion and marketing of agricultural imputs were discussed by several participants. Several speakers said that though coordinated marketing of all

the agricultural inputs was essential, it might not be easy to implement this idea without careful planning and cooperation of all the agencies. A view was expressed that a corporation or a consortium should be set up to promote the use of all inputs so that awareness among farmers was increased.

It was also felt that synchronization of the efforts of all the marketing agencies involved in agriculture was necessary. Formation of a coördination committee including representatives of the Fertilizer Association of India, the Pesticides Association of India, machinery seed and financial institutions was suggested.

Difficulties experienced by dealers and wholesalers in stocking all the inputs were brought out. It was also stated that dealers with meagre eductional background could not be expected to advise farmers about correct use of fertilizers and other inputs. It would be advisable to entrust this job to trained personnel of the concerned agencies.

One of the participants suggested that the coordinated marketing of inputs could be undertaken in two stages. In the first stage integrated marketing only of seeds, fertilizers and plant protection chemicals should be tried and once this was successfully undertaken, other inputs could also be added.

Since fertilizer happened to be the chief input of agriculture, it was felt that the initiative in establishing a coordinated approach in marketing of inputs should come from the fertilizer industry.

It was pointed out that in some of the States, cooperatives were still stocking only fertilizers. In order to encourage them to stock other inputs also, commercial banks should extend suitable credit facilities.

[Benoy K. Banerjee]

Haldia Complex

For the success of a project like Haldia complex, which needs massive investment and embraces various branches of technology, requires foresight, pre-thinking, planning and proper execution. Before start of the actual project people from various branches of technology should gather together and pool their experience and expertise that can guide the project authorities in visualizing the project in its proper perspective and plugging the pitfalls. The papers submitted at the three-day (Nov. 5-7, 1971) seminar on Haldia complex held at Calcutta must have proved useful to project authorities as diverse subjects like development of port, setting up of petrochemical complex, fertilizer factory and possibility of ancillary industries were covered.

The topic of the first session was development of port, ship-building industry and water supply to the complex, In a paper entitled 'Development of Haldia Port and its Industrial Complex' Mr. K. N. Sen told how the idea of Haldia complex was conceived and narrated the step by step development of the events that shaped the present form of Haldia project. He informed that the first phase development of the dock system provides seven berths one each for coal, iron ore, rock phosphate, heavy lift-cum-container, grain-cum-general cargo, finger jetty, oil (riverside). The distinctive feature of the Haldia dock will be that all these berths will be equipped with high speed mechanical facilities and all equipments will be procured in India for the first time. The Mining & Allied Machinery Corporation Ltd. Durgapur has been awarded a turn-key contract for the manufacture, supply and commissioning of the ore and coal handling plant.

The requirement of water for Haldia complex is estimated to be about 50 mgd. in 1982 giving rise to 100 and 240 mgd. by 1995 and 2070 respectively. The present demand of water can be conveniently met by ground water resources. But in future it is proposed to draw river water from Uluberia, 30 miles upstream of Haldia where the river water will be potable all around the year on completion of Farakka Barrage in 1972 when continuous head water supply from the Ganges would be assured. The cost of developing the available ground water resources to the extent of 50 mgd will amount to Rs. 3.5 crores; and that of the river water Rs. 12 crores for the first phase supply of 45 mgd and Rs. 11 crores for further 45 mgd in the second phase. The water supply problem has been studied in more detail by Mr. B. Maitra in another paper.

The power will be the prime necessity of complex like Haldia where dock, refinery, fertilizer project and other ancillary industries are to be fed. The total demand by 1974-75 is estimated somewhere 32,000 kV from the present drawl of 1400 kV. Fertilizer project and refinery will have their captive generating plants. In a paper by Shri B. N. Banerjee, the role played by West Bengal State Electricity Board in supplying electricity to Haldia complex is explained.

For a designated traffic in a port for several commodities a system can be conceived between the commercial need for moving them by bulk-carriers and the technical and economic feasibility of deepening the approach channel. Possibility of developing a mathematical model for such system is discussed by A. N. Biswas of Calcutta Port Commissioners.

Liquid natural gas (LNG) finds many industrial applications as feedstock in fertilizer and petrochemical pro-

jects, as fuel in engineering and metallurgical industries, and as substitute for high sulphur fuel oil or coal thereby eliminating the possibility of atmospheric pollution. Mr. M. J. M. Lyal and Mr. P. K. Bose of M/s. Indian Oxygen Ltd. outlined the scope for terminal facilities for LNG at Haldia and suggested the import from the countries like Middle East and South East Asia who are surplus in natural gas. The paper also described the LNG project of Algeria/UK as an example of the practicalities of natural gas liquefaction, transportation, storage and distribution. Haldia has good deep water facility and in the view of authors this place could be developed as a centre for pipe line distribution of natural gas to metallurgical/chemical industry in and around Haldia and natural gas can also be piped to the existing steel and fertilizer project throughout W. Bengal and Bihar.

Mr. P. C. Mittra of Calcutta Port Commissioners feels that there is a strong case to have a shipyard at Haldia. Keeping in view the tonnage in operation, on order and scheduled to be built at the Hindustan & Cochin Shipyards it is calculated that there will be shortfalls in shipping tonnage to the extent of 0.51 million tons d.w in 1975-76 to 0.78 million d.w. in 1980-81. The author suggests that we may concentrate on oil tankers and bulk carriers at Haldia with Visakhapatnam confining its activities to the production of general cargo ships. The building of ships at Haldia should also be co-related with the work in order that these two yards may specialise in different merchant ship types to minimize cost of production. The planning of the shipyard set-up should however be such in each of these two yards that naval construction should be possible. Then the author discussed possible location in the river and its influence on the industry.

In a paper entitled 'Bulk Transportation at Sea the Changing Pattern and its Implications' three different aspects of bulk transportation have been considered. Firstly, some recent trends in the development of specialized ships have been dealt with. Secondly, the economic aspects of this trend have been considered in relation with cost of transporation and efficiency of loading, unloading and distribution facilities. Thirdly, the essence of need based development has been stressed and certain important dock development projects in other parts of the world have been presented. The emergence of Bangladesh may give impetus to the shipping industry since bulk transportation of coal, iron, cement, etc. is possible through Haldia port.

Haldia dock project ushers in a new era in terminal operation and cargo-handling technology in India. There is indeed a variety of choice for selection of each type of these equipments and a proper selection based on judicious study of all the factors of operational requirement, economics, availability of engineering and industrial resources in terms of technical know-how, material, maintenance, etc. is of vital need for the successful implementation of any such project. Sri S. R. Bose analyses the situation and discussed the ways to meet it. He suggests that the specification of plant and equipment should be drawn keeping in view the indigenous suppliers and due attention must be given to the erection and maintenance problems of sophisticated eauipments. The absence of R & D setups with indigenous suppliers is one of the biggest drawbacks. This calls for immediate setting up of R & D cells with experienced and creative design engineers whose sole function would be to produce economic and customer-oriented designs and to get mixed up with day to day commercial and production activities. Top level coordination and proper delegation of authority which is required for any successful project, in Haldia project is also essential.

The second session dealt with refinery and fertilizer project. Haldia refinery will process 2.5 million tonnes/year crude obtained from Aghajari (Iran) and will produce the various products. In a paper 'Haldia Refinery' the author has informed that for the Haldia refinery, Messrs Technip of France and Industrialexport of Rumania are giving their assistance in the process design, engineering design and equipment supply for the Fuel and Lube sectors of the refinery respectively. The collaborators have agreed to associate the Indian Institute of Petroleum and Engineers India Ltd., in the development of the project. The agreements signed by the Government with the foreign collaborators were transferred to the Indian Oil Corporation for their implementation. For units needing specialized know-how like naphtha pretreatment and reforming, kerosene hydrodesulphurisation French Institute of Petroleum and Indian Institute of Petroleum are the process licensors, for sweetening of LPG and naphtha, Universal Oil Products (U.S.A.); for hydrofinishing of lube base oils French Institute of Petroleum are process licensors. The author, Shri T. S. Krishnamurthi, has further described the various process units in detail.

The establishment of the petrochemical complex along with the refinery will bring about a rapid and balanced industrial growth in the region. Numerous chemical intermediates including coal chemicals from Durgapur area will be available for the manufacture of diverse types of end-use products in medium and small scale sectors. In a paper 'The role of Haldia Refinery in the Petroleum Industry of India' the authors have presented brief account of the present status and future plans for development of

the petroleum industry in India with special reference to Haldia Refinery complex. The consumption and the demand growth of the major petroleum products in the coming years have been reviewed. The special features of the Haldia Refinery project and the possibilities of manufacture of a wide range of lubricants, greases, special oils, solvents and bitumen products have been indicated. The trend in the growth of the petroleum-based chemical industries, the outline scheme for the production of major petrochemicals and present demand and the estimated requirements at the end of the fourth plan period have also been discussed in the paper.

Import substitution is a long felt and much talked about subject. Mr. J. D. Choudhury of Indian Oil Corporation Ltd., has described how in a systematic way the import substitution in oil refineries is being carried out. He has stated the steps taken in this direction and claimed that indigenous content as percentage of total project cost in case of Madras refinery was of the order of 60.8 per cent whereas in case of Haldia, this is going to be in the order of 70 per cent of the total project cost. This import substitution could have been further increased if Haldia project were not compelled to import about 1200 MT of steel plates for a c.i.f. value of about Rs. 1.3 crores due to steel scarcity in the country.

A technoeconomic survey of Haldia fertilizer complex is made in a paper submitted by Planning & Development Division of FCI Ltd. As rock phosphate is to be imported and there is a marketing area in eastern part of northern zone and eastern zone, Haldia is a suitable place. Moreover, by-products like soda ash (used in glass industry) and methanol have a ready market in eastern zone. The product pattern proposed in the paper is urea, nitrophosphate, soda ash and methanol. The authors have given a detailed account of processes to be adopted in various plants. Both ammonia and nitrophosphate plants will be using the processes which for the first time are being tried in India. In ammonia plant fuel oil will be gasified by non-catalytic partial oxidation at comparatively higher pressure. In case of nitrophosphate plant where production of high nutrient is envisaged a sulphate recycle process developed by Stamicarbon is being used. The process adopted in Haldia for soda ash is unique because of the use of waste by-product chalk from phospho-gypsum, instead of natural limestone. The technique has been jointly developed by M/s Polimex of Poland and P&D Division of FCI in their own pilot plant at Sindri. The steps involved are: (1) lime preparation, (2) preparation and purification of the salt brine, (3) ammoniation of brine and (4) calcination of sodium bicarbonate. The authors have given the raw materials requirement for the fertilizer plant and costs of end poducts derived are: urea—Rs. 386/te; nitrophosphate—Rs. 408/te; soda ash—Rs. 524/te; methanol—Rs. 500/te. In another paper by P&D Division, 'Survey of Gas Purification Processes for Haldia Fertilizer Complex' an analysis of different alternative routes for the purification of crude gas into pure synthesis gas for the production of liquid ammonia, has been made with a view to selecting the most suitable route. It has been shown that the two-stage methanol wash followed by liquid nitrogen wash economically fulfils the requirements of the proposed process conditions at Haldia, having a gas purification capacity equivalent to 600 tepd of ammonia and 125 tepd of methanol. Possibilities of by-product recovery have been studied and it has been indicated that the sulphur recovered from sulphur bearing fuel oil, as hydrogen sulphide, can be used for sulphuric acid production. Argon recovery from air separation plant and liquid nitrogen wash plant have also been considered.

There were three papers in the third session on the feasibility of petrochemicals industry at Haldia. First paper, 'Planning of Petrochemical Industries at Haldia', outlined factors to be considered for establishment of petrochemical industries in eastern India. Based on the likely demand of major petrochemical products, a list of possible petrochemical industries has been drawn. Availability of the basic raw materials such as naphtha, propane and light crude oils is reviewed in the light of present stage of technology. A brief indication regarding economic capacities of some of the units as also the range of capital investments has been presented. The techno-economics for establishing a synthetic rubber plant at Haldia are studied in more detail. Medium and large scale downstream industries which can be based on the products of a central petrochemical plant at Haldia are discussed in brief from the point of view of employment and revitalization of chemical industry in eastern region.

The use of synthetic fibres throughout the world for garments and industrial purposes like tyre cords, conveyor belts, etc. is fast increasing. There is a scope for installation of additional capacities of 21-22 thousand tonnes of nylon and 7 to 7.5 thousand tonnes of polyester fibre to meet India's demand of synthetic fibres in 1973-74, say Messrs B. B. Ghosh and A. Sural. Therefore, there is a need for setting up of synthetic fibre plant at Haldia based on 500,000 tonnes naphtha cracker unit.

At the time of and immediately after their production. fuels, propellants, fuel oils, lubricants, and other products made from hydrocarbon fractions should be protected from ageing by substances inhibiting oxidation.

Because, when hydrocarbon fractions or their mixtures are stored or used under the influence of heat, oxygen of the air, light metal traces of copper, vanadium etc. they not only become discoloured or turbid, but sediments are formed as well. Sri S. K. Bhatnagar of Bayer (India) Ltd., has reviewed the various antioxidants required and used in oil industry.

As high grade iron ore and coal are abundantly available in eastern region a process using coal as reductant would be suitable for sponge iron plant at Haldia. In a paper submitted by Sri S. S. Das Gupta economics of sponge iron plant with annual capacity of 1,2,3 and 4 lakh tonnes have been examined and found that plant lower than 2 lakh tonnes capacity is not profitable while plant with 4 lakh tonnes capacity is most attractive. As Government of India has restricted the capacity of sponge iron plant to 3 lakh tonnes per annum the plant of this capacity as per author's findings will also be quite attractive with gross return of fixed investment in the region of 30 per cent and a pay out period of 2.5 years. To meet India's growing demand of zinc and copper indigenous sulphide ore is to be augmented with imports. In a paper submitted by Mr. S. K. Dey and Dr. T. K. Roy a suggestion has been made for setting up a plant at Haldia using hydrometallurgical process for simultaneous leaching of zinc and copper and precipitation of elemental sulphur. The recovery of zinc and copper by electrolysis and sulphur recovery by flotation assuming plant capacity 20,000 tonnes/year each have been studied by authors and stated that such integrated plant will save about Rs. 800 million tonnes per year in foreign exchange.

Many ancillary industries like food preservation, building material, plastic products can be set up by utilizing the intermediates or by-products from the fertilizer complex at Haldia. This will meet the market demand and help to combat pollution. Sri H. C. P. Sinha has catalogued the ancillary industries which can be based on acids like sulphuric, phosphoric, nitric and phosphogypsum, soda ash, ammonia, urea, etc.

In Sri Nandan Bhattacharya's view educated and technically qualified men and women of West Bengal form the most important constitutent of the electronic industry; the author feels that an export-oriented electronic industry at Haldia can flourish. He further stated that manufacturing electronic equipment in 'Free Trade zone' in Haldia is cheaper than in Japan, USA, Europe, and Hong Kong.

To cater to the needs of complex like Haldia, small scale industries have a good prospect. Some industries will be needed in the course of the construction, some will play the supplementary/complementary role, others will utilize products, by-products or industrial wastes. Those rendering consumer-service will also be required. Mr. S. N. Shivapuri has given an indicative list of primary, secondary, tertiary and quaternary industries.

Dr. S. K. Sirkar in presenting a few stray thoughts asked the gathering to consider problems like industrial wastes, preventive maintenance, creation of additional workshop facilities, planned township beforehand. He also suggested to explore the possibility of putting up a blast furnace of suitable size for manufacturing pig iron.

Sri A. N. Bose, Industrial Economist of CMPO has enumerated the difficulties faced by Calcutta port and discussed the socio-economic significance of Haldia development. Mr. S. S. Sen, President of Indian Engineering Association pointed out many advantages to India if Haldia is made "Free Trade Zone". Similar experiment at Kandla port failed because of absence of industrial development in that area and no support from the hinterland, lack of shipping facility at Kandla since port does not fall on the normal route of the shipping line. Haldia is free from all these drawbacks so it can make significant contribution towards increasing the export of Indian engineering goods and other manufactures.

To sum up the papers presented to seminar are informative and give the glimpses of a project that will take shape at Haldia. The pre-print would have been more attractive had a little more attention been paid to editing, proof reading and binding.

[S. A. Kulkarni]

Reviews

Start-up Problems of Fertilizer Plants

The Fertilizer industry being highly capital-intensive quick start-up ensures the beginning of early returns on investment. Delay in start-up due to trouble may cause complete or partial stoppage of plant and restart-up takes again a number of days in extensive replanning leaving aside the highly significant aspect of loss of production from delay. A group discussion on start-up problems of fertilizer plants was held by the Fertilizer Institute of New Delhi in collaboration with the Northern Regional Centre of the Indian Institute of Chemical Engineers at Shriram Industries, Kota during Nov. 14-15, 1970. Representatives from various important firms of India associated with fertilizer industries took part in the discussion and expressed their views on the start-up problems in fertilizer plants and how to eliminate them. Altogether 13 technical papers were read by the participants and they discussed on: (1) problems arising out of defective design, faulty equipment and faulty construction, (2) problems arising out of faulty operation and human error and (3) problems connected with personnel.

Sri H. A. Bhatta of Shriram Chemical Industries, Kota discussed the problems due to design and suggested that experienced operating personnel should associate themselves during the design stage where they can point out some of the defects and suggest improvements. The second problem is with defective machinery and the required spares. The problem with machinery manufactured in the country is that it is sold in seller's market and manufacturers here are least concerned about quality. To overcome the problems of construction it has been suggested that production people should be intimately connected with the construction. By trial and error indigeneous substitution of spares and machinery has to be developed. Planning has also to be made for safety. Sri T. Singh of Shriram Chemical Industries suggested that a control pool of experienced people with specialists should be formed who would be associated with every new plant which is going to be started. On the basis of their experience they would solve start-up problems.

Kellog and ICI have published their experiences on start-up problems of new ammonia plants where it has been reported that about 40 per cent of the start-up problems faced by Kellog and 61 per cent by ICI are due to faulty equipment. Faulty design is practically the same which is 10 per cent in the cases. The faulty operation and human error have been given as 30 per cent by Kellog and 13 per cent by ICI. ICI have reported that faulty erection has caused 16 per cent of start-up problems whereas Kellog experienced 20 per cent start-up problems due to faulty erection. Almost all speakers told that an experienced member of the operation team should be put along with constructional team towards the completion of the construction to ensure that the construction has gone as per the standard condition laid down as design.

Being a developing country, we are tied by credits. In setting up a fertilizer plant with foreign collaborators we are not left with much alternatives but go for a certain type of process and equipment tied with particular credit. One of the drawbacks in this type seems to be that the supplier at times dictates its terms, even in case of selection of equipment and process. Roughly 40 per cent of the equipment are still coming from foreign countries. Efforts are being made in FCI to get only the bare requirements of the equipment and get mostly raw materials from outside for fabrication of the equipment in this country. Indigenous skills and talents available are of limited order. In planning and execution, all conceivable problems have to be foreseen to get away the difficulties during start-up and commissioning stages. Participants in their papers discussed start-up problems in various fertilizer plants in India and made some recommendations to eliminate them.

Books

Polyester Resins by J. R. Lawrence (Van Nostrand-Reinhold Co., New York), Pages ix & 251.

This book presents an excellent semi-technical review of polyester resins from the standpoint of chemistry, curing and diversified applications. The presentation is aimed at giving better understanding of the materials and how they are used. The book will be valuable to plastics workers e.g. to design engineers, producers and manufacturers of packages, teachers and students at technical

schools, etc. The book describes history, chemistry of polyester resins, general properties, formulations, manufacturing, curing, molding and laminating processes and coating applications. This book is eminently suitable for all those who are interested in plastics. The book is brief but has covered the most important developments in plastic industry in a single volume.

Vijay Mohan Bhatnagar,
Iroquois Chemicals Ltd.,
Cornwall, Ontario, Canada

Polymers—Structure and Bulk Properties by P. Meares (D. Van Nostrand Co. Ltd., London), Pages xi & 381.

This highly interesting book provides a readable account of current knowledge about the physical and mechanical properties of bulk polymers in relation to their molecular structures. The author, a senior lecturer at Aberdeen University, has made an excellent attempt throughout to explain all matters of principle clearly and qualitatively. The book will be very useful to teachers and advanced students in colleges and universities, who are working in polymer field, and also to polymer researchers in industry. The author has covered several important topics under the following headings: the chemical basis of polymers. The microstructure of chain molecules, molecular weight and branching, the crystallinity of polymers, The fusion and crystallization of polymers, elastomers and the thermodynamics of rubber-like elasticity, the statistical thermodynamic theory of high elasticity, practical aspects of elasticity theory, the nature of visco-elasticity, the glassy state and glass transition, retarded high elasticity, diffusion of gases and vapours in polymers, and irreversible deformations.

Vijay Mohan Bhatnagar, Ontario, Canada

Polymers and Resins by B. Golding (Van Nostrand Co. Inc., Princeton, USA), Pages viii & 744.

This book can be recommended as a textbook to any college and university. The author has included the theory, chemistry, fabrication, and applications of polymeric and resinous materials in a highly readable form and in a logical manner. Besides covering plastics, the book also includes fibres and elastomers. Hence. the book can be used as a text regardless of the particular field of interest of the teacher. The main topics, which cover several fields associated with these headings, included in the book are: definitions, formation, mechanical and chemical behaviour, Characterization of polymers, methods of polymerization, natural and modified natural products, synthetic condensation products, synthetic addition products, effect of molecular structure upon mechanical behaviour, fabricating and processing, and applications.

These books are highly recommended to every Indian college and University. Indeed they will be excellent additions to the library of anyone who is interested in polymer science.

Vijay Mohan Bhatnagar, Ontario, Canada

Introduction to Polymer Science By L. R. G. Treloar (Published by The Wykeham Science Series, Taylor and Francis Ltd., London), Pages viii + 183, 1970. Price £ 1.50

This is one of the best books on polymer science for the beginners. It clearly shows how the physical properties of the principal types of polymers can be understood in terms of their basic molecular structure. The chapters include 1. From rubbers to glasses. 2. The polymer molecule: its size and form. 3. Why is rubber elastic? 4. The molecular network. 5. The glassy state. 6. Crystallization phenomena in rubber. 7. Crystalline polymers. 8. Fibres and fibre formation. 9. Strength and fracture. 10. Water absorption and swelling, and 11. Elastic liquids.

These chapters should surely enable the reader to understand not only the characteristic differences between the various kinds of polymeric materials of industrial importance, but also the broad differences in both structure and properties between polymeric and non-polymeric substances. Indeed this book is a very useful addition to the literature on polymer science and one which will be of great assistance to students, teachers, researchers, and technologists who are in any way concerned with polymers processing, physical properties or manufacture. It is strongly recommended to all libraries in India and to individuals interested in polymer science.

V. M. Bhatnagar,
Ontario, Canada

Notes & News

Ammonium Polyphosphates

Use of ammonium polyphosphates as fertilizers permits the attainment of high P_2O_5 concentrations in compositions which have higher water solubility than materials based on orthophosphates. In addition, polyphosphates are excellent sequestering agents and therefore allow the production of clear liquid fertilizers, which are stable and devoid of insoluble material and which may contain considerable quantities of micronutrients without any precipitation occurring.

Traditional methods of manufacturing ammonium polyphosphate involve the use of superphosphoric acid obtained either directly from elemental phosphorus by the thermal process or by evaporation of wet process acid.

French firms Kaltenbach and Cie and Establishments Gardinier of Paris announced a recent process where normal 52-54 per cent P_2O_5 wet process phosphoric acid is used as feedstock. The use of normal wet process acid has two main advantages. These are firstly the neutralization reaction with ammonia is exothermic and therefore allows the economy of using the heat generated for the purposes of concentrating the reaction feedstock, and secondly that simultaneous neutralization reduces the corrosion problems normally associated with the concentration and polymerization of phosphoric acid. Along with other direct ammonium phosphate techniques, the Kaltenbach-Gardinier direct process is extremely simple in design and requires only minimal control and operating labour. In the Kaltenbach-Gardinier process phosphoric acid passes down the combined evaporator preneutralizer countercurrent to a stream of excess ammonia and steam issuing from the reactor. Here the acid is concentrated and undergoes preliminary polymerization and neutralization. Excess steam given off in the evaporator as a result of the neutralization reaction is condensed in a water cooler and returned to the 10 : 34 : 0 solution tank. This is the only potential effluent from the process and since it is recycled, all pollution problems are obviated and process losses are reduced to negligible levels.

The concentrated and partly neutralized acid is fed to the reactor into which gaseous ammonia is injected. Ammoniation takes place at 235°-240°C and the reactor is maintained at this temperature by virtue of the heat of the exothermic reaction. Steam, loaded with excess ammonia, is driven off from the molten polyphosphate and provides the necessary heat for the preconcentration which takes place in the evaporator/preneutralizer.

Molten ammonium polyphosphate is the reactor product and this can be utilized in the preparation of a 10 : 34 : 0 place in a separate stirred vessel, and the heat content of the 10 : 34 : 0 product is used to evaporate liquid ammonia prior to its introduction into the process in a gaseous form.

Owing to its great simplicity and flexibility, the process is stated to be extremely easy to operate, requiring only a single operator, and is characterized by a complete absence of environmental pollution.

By precise process control, the Kaltenbach-Gardinier technique allows the production of polyphosphates with degrees of polymerization anywhere between 30 and 70%.

[*Phosphorus & Potassium*, No. 49, 1970, p. 18]

New Phosphoric Acid Technology

1. *Cation-exchange to two phosphoric acid processes.*

Two new processes recently patented in the U.K. both involve the use of cation-exchange resins to produce phosphoric acid with a low level of impurities.

Multi-minerals Development: One of the processes, developed by Multi-Minerals Ltd. of Canada, involves the digestion of phosphate rock in phosphoric acid to yield monocalcium phosphate as a crystalline intermediate, followed by ion-exchange resin. The basic steps are shown in the diagram. Acidulation with recycled phosphoric acid takes place at between 85 and 105°C, preferably above 95°C, there being an excess of acid of the order of six times the stoichiometric quantity.

The monocalcium phosphate so formed is crystallized by lowering the temperature some 10°-15°C, filtered, and then passed, together with unseparated solid impurities, to a cation-exchange column. The phosphoric acid is produced simultaneously with the conversion of the exchange resin to the calcium form. Part of the product acid is recycled to the wash liquour storage tank and eventually serves as make-up to the acidulating solution.

Solids are washed from the resin, which is then regenerated to the H-form by exchange with any available inorganic acid, thus indirectly allowing the use of an acidulant which would not normally be suitable for phosphate rock digestion.

Montedison Process: The second process, developed by Montedison SpA of Italy, claims to avoid the need for the complex and specialized equipment necessary for normal wet phosphate processing and provides for operation at ambient temperature. However, it has the disadvantage of only producing dilute solutions of phosphoric acid. In contrast to the process already described, the Montedison invention entails the use of an ion-exchange resin directly to extract the phosphate content from rock phosphate without the use of a digesting acid.

Basically, mineral phosphate is treated in aqueous suspension with a cation-exchange resin in the hydrogen form to produce a reaction approximated to by the following chemical equation:

$$10RH + Ca_5(PO_4)_3F \rightarrow 5\,Ca(R)_2 + 3H_3\,PO_4 + HF$$

By using an excess of exchange-resin, it can be ensured that the resulting aqueous phosphoric acid solution is free from cationic impurities. A resin particularly suited to this purpose is stated to be obtained by the sulphonation of styrene divinyl benzene copolymers. Speed of reaction depends considerably upon the fineness of grinding but, for phosphate rock with a particle size less than 100 mesh, the reaction is complete in about one hour.

After separating from the resin, the phosphoric acid solution produced possesses an H_3PO_4 content of around 2 per cent by

volume but, if filtration wash waters are recycled to the digestion stage, this content can ultimately be increased to 8 per cent; the resin is regenerated by contact with a strong mineral acid, such as hydrochloric. Anionic impurities are not eliminated from the acid during processing—and it is questionable, therefore, how corrosion difficulties are alleviated but if hydrofluoric acid is present in the product, this can be removed by heating. The process is readily adaptable to the production of technical and detergent phosphates.

2. *Integrated Phosphoric Acid Process from Allied Chemical Corp.*

The hydrochloric acid attack process for the manufacture of phosphoric acid gives rise to the by-production of calcium chloride brine and, as with other wet phosphoric acid systems, the advantages have long been recognized of techniques by which the acidulant can be regenerated from the by-product. Although partial success in this respect has been achieved with sulphuric acid and nitric acid-based systems, it has hitherto been commercially impossible to successfully regenerate hydrochloric acid, or hydrogen chloride, for recycle from calcium chloride brine. It is known that hydrogen chloride can be generated from magnesium chloride by a thermal hydrolysis technique, commonly known as the Aman process, developed in Israel, but a similar route using calcium chloride has not yet been perfected, since the temperature requirement in this case is considerably higher and, moreover, calcium chloride does not hydrolyze very efficiently at elevated temperature, as does magnesium chloride.

In this context, a completely integrated recycle process for the production of phosphoric acid by hydrogen chloride attack has been developed by Allied Chemical Corp. of the U.S.A., which involves regeneration of hydrogen chloride from calcium chloride brine by reaction with silica or alumina. The reaction of calcium chloride with silica or alumina in the presence of water has been known for some time, but previous attempts to carry out the operation on a large scale have not been successful. The Allied process claims to be effective and economical, and has the advantage that calcium silicate or calcium aluminate—both of which are basic ingredients of Portland and other types of cement—are the process by-products.

Key to the process is a fluidized bed reactor in which silica or alumina, or a mixture of both, are reacted with calcium chloride brine. Various silicates and aluminates of calcium are produced, in reactions typified by the following equation:

$$2\,CaCl_2+SiO_2+2H_2O \rightarrow 4\,HCl+\underset{\text{dicalcium silicate}}{Ca_2SiO_4}$$

The hydrogen chloride, simultaneously evolved, may subsequently be used in gaseous form to acidulate phosphate rock. According to the investigation, acidulation takes place in a series of towers in which the acid gas passes counter-current to the flow of finely divided phosphate rock slurry. After completion of the acidulation step, phosphoric acid is recovered by solvent extraction and the remaining calcium chloride brine is recycled to regenerate the gaseous acidulant, thus completing the reaction cycle. A flow diagram of the system is shown.

The fluidized bed reactor is made from carbon steel and lined with refractory brick; the preferred operating temperature is between 700° and 950°C. Optimum reaction conditions are obtained when the proportion of calcium chloride in the reactor is not more than 15 per cent by weight, with a retention time greater than two hours.

Flue gas from the reactor is freed from particulates in a cyclone separator and then serves to preheat the process air feed to the base of the reactor. The preheater operates at around 400°C, and the partially cooled flue gas, containing something like 10 per cent hydrogen chloride, is fed to the first acidulation tower, which is lined with acid-resisting brick. It is here that the acidulation of the rock slurry is completed, and the gas stream is cooled further to about 100°C.

The acidulation towers operate at essentially atmospheric pressure and 90-100°C. Reaction conditions dictate the use of rubber linings and polypropylene internals in the towers. Acidulation takes place countercurrently, the slurry preferably containing 20-40 per cent of rock—entering at the top and leaving at the bottom, whilst the gas stream enters at the bottom and leaves at the top. Flue gas emitted from the final acidulation tower is practically completely depleted of hydrogen chloride and is vented directly to the atmosphere.

Phosphoric acid is isolated from the acidulated slurry by solvent extraction followed by recovery by water-washing. Suitable solvents to separate phosphoric acid from the associated calcium chloride brine include C_4 and C_5 alcohols, triethyl phosphate and certain amides; iso-amyl alcohol is preferred.

[*U.K. Patents*, Nos. 2, 174, 204, 1, 172, 293 and 1, 167, 461; *Phosphorus and Potassium*, No. 49, 1970, p. 20]

CSIR 1970

The annual report for 1970 of the Council of Scientific and Industrial Research, India, indicates that the research programmes of the laboratories continued to be project-oriented towards industrial advancement of the country. Over 1850 research projects, comprising 1600 applied and 250 basic, were under investigation which included 350 projects sponsored by or taken up at the instance of industry and other organizations.

Physics and Electronics: Techniques for the fabrication of TV picture tubes have been worked out at NPL New Delhi; and following the successful development of helium-neon laser, a pulse type argon ion laser has been developed using indigenous material. A portable ultrasonic device for aiding the blind, which is better than the conventional blind-aid devices, has been developed by NPL. Another achievement is a 6-digit 2-function electronic desk calculator fabricated mostly from indigenous components. The National Aeronautical Laboratory has also developed a calculator using integrated circuits; it is capable of addition, subtraction, multiplication and division on 8-digit number with results displayed to 16 digits. Such calculators are presently imported.

In view of the trend that integrated circuits are fast replacing discrete components in electronic equipment because of the lower cost, smaller size and weight and lower power requirements, the Central Electronics Engineering Research Institute has developed techniques for the fabrication of integrated circuits of silicon monolithic type. Silicon planar transistors and diodes have been designed. N-P-N silicon epitaxial transistors produced by the CEERI were found satisfactory by the industry.

Chemical Technology: At the instance of the Jammu and Kashmir Government processes for the manufacture of rayon and tyre cord grade pulps from bamboos, eucalyptus and Kashmir sprue have been developed at NCL. Following the development of an electrochmecial process for phosphatizing, Central Electrochemical Research Institute has set up a pilot plant for anodic phosphating of steel. This Institute has developed a nickel cadmium sealed button cell. RRL Hyderabad has commissioned a prototype furnace for the production of silicon carbide. RRL Jammu has developed a process for plaster of Paris suitable for thin layer chromatography using local gypsum. CBRI Roorkee has developed the technology, for the manufacture of gypsum plaster and plaster pro-

ducts from gypsum anhydrite (by-product in the manufacture of hydrofluoric acid). It has also worked out a process for vitrified bricks of high compressive strength and low water absorption from alluvium soil of Kandla harbour region.

Process details for the manufacture of special mud thinners used in oil well drilling beyond 10,000 ft. depths have been developed by the Central Leather Research Institute, using myrobalans. Treatment of high sulphur lube base stocks from Madras refinery for manufacture of transformer and white oil has been investigated by the Indian Institute of Petroleum in order to select siutable feedstocks and establish process conditions.

Coal, Fuels, Metallurgy and Mining: A scheme for the utilization of sub-bituminous Singrauli coal has been prepared by CFRI to produce electricity, gas, washed coal, domestic and industrial fuels for metallurgical industries, fertilizers, carbo-chemicals, tar chemicals and carbon products. A new parent coking seam (VIII A) has been located in Sudamdih area. Two thick seams having high caking index have been encountered in the Barren Measures of Jharia coalfield. In the Jarangdih block of E. Bokaro coalfield primary coking coals have been developed. CFRI has developed processes for (i) making spherical smokeless domestic fuels from coal washery rejects, etc using pelletizing technique; (ii) selective preparation of coal by pneumatic separation upto 5 te/hr, and production of hard, composite quartzite briquettes from coke breeze, lignite char, etc. RRL Jorhat has developed a process for manufacture of carbon black from Assam coal for which a 250 kg/day pilot plant is being designed.

The characteristics of crude oils from Nahorkatiya, Lakwa and Rudrasagar fields in Assam have been studied by IIP Dehra Dun and the data obtained have been adopted by the Indian Oil Corpr. Ltd. for its new refinery in Assam. IIP has also developed a highly effective alkyl nitrate type additive (Catal E) for improving cetane number of diesel oil from Assam crudes.

NML Jamshedpur has studied the extraction of nickel from Sukinda nickel ore (Orissa) and furnished technical data to the Chemical and Metallurgical Design Co. (P) Ltd. In the context of the limited resources of coking coal, NML is developing a process for tonnage quantities of prereduced pellets and sponge iron.

Glass, Ceramics, Leather and Other Technologies: Central Glass & Ceramic Research Institute, Calcutta, using indigenous raw materials have developed ceramic water filter candles for obtaining drinking water free from harmful bacteria. Another process developed by CGCRI relates to the conversion of indigenous Ca-Mg type bentonite to Na-type for use in vitreous enamelling industry. This product is comparable to the imported material. Other achievements relate to: (i) glass composition for sealing with ordinary mild steel electrodes and ferrules (ii) a novel method for producing mechanically strong and leakproof seals having high electrical resistance.

Tie and dye type leathers developed by CLRI Madras have been successfully adopted in several tanneries at Calcutta, Bombay, Madras, etc. These leathers with floral designs for clothing have a good demand in the international market.

Based on the revrese osmosis technique a desalination plant for production of 3400 litres of salt free water/day has been installed by the Central Salt & Marine Chemicals Research Institute. This Institute has also developed cation and anion type of interpolymer membranes used in electrodialysis plant for desalination of brackish water.

Food and Fruit Technology: A toxin-free protein-rich mustard flour (protein 50 per cent) has been produced by the Central Food Technological Research Institute. Processed edible sesame flour (protein 65 per cent) has been developed. Other products developed by CFTRI include: air-dried mutton mince containing 50 per cent vegetable protein meat and mutton based sausages; activated clays sorbed with fumigants for preventing hot spots which occur due to migration of moisture in the foodgrains stored in metal tins.

Instruments and Devices: Central Scientific Instruments Organization has developed: (i) foetus monitor for detecting the condition of foetal heart in pregnancy from the tenth week onwards; (ii) time interval counter suitable for accurate measurement of time interval between two events, such as the problem encountered in the determination of the velocity of missiles (iii) bubble chamber scanner used for experimental study of sub-atomic decays and interactions; (iv) focimeter used for the measurement of vertex power, prismatic dioptric power, etc.

Engineering and Engineering Industries: Some of the important investigations of the Central Road Research Institute are: (i) corrective measures for landslides on behalf of Border Roads Organization (ii) evaluation of the capacity of reclaimed fill to take up loads of ore stacks safely at Madras Harbour Reclamation Project: (iii) foundations of the ore handling yard at the Outer Harbour Project; (v) raising the standard of Kalka-Simla Road.

Experimental investigations on the behaviour of partially prestressed concrete members, prestressed to various degrees have shown that (i) use of partially prestressed concrete in place of fully prestressed concrete results in a saving of 21-37 per cent high tensile steel; (ii) partially prestressed members give better performance under service loads. The switch-over from fully prestressed concrete to partially prestressed concrete will lead to substantial savings in materials and costs.

A high pressure vessel fabrication rig involving the design and development of its constituent units has been fabricated by the Central Mechanical Engineering Research Institute, Durgapur. The know-how for the manufacture of a continuous belt weighing machine used in cement, fertilizer and processing industries has been developed.

Testing of the various configurations of an advanced technology aircraft, being designed by the Hindustan Aeronautics Ltd., in the 4-ft. trisonic wind tunnel was completed at the National Aeronautical Laboratory. Rocket models on behalf of the Space Science and Technology Centre, Thumba and defence models were also tested.

A feasibility study for the Calcutta city's refuse was completed by the Central Public Health Engineering Research Institute giving recommendations with regard to sanitary land fillings, incineration and a mechanical composting plant of 200 tonnes/day capacity.

Research Utilization and other Data: During 1970, 33 patented processes and 54 non-patented processes were referred to the National Research Development Corpn. for commercial utilization. 53 processes have been released to industry, bringing the total number released so far to 416. 192 processes are under commercial or trial production.

The revised budget of CSIR for 1970-71 (in lakhs) is capital Rs. 728.168, Recurring Rs. 1536.501. Total scientific and technical staff 9444; research fellowships 2992, research schemes 778, pool scientists 323, retired scientists 80, emeritus scientists 15.

[*CSIR News*, **21** (18) (1971), 137]

Performance of F.C.I. Ltd. during 1970-71—Chairman's Statement

During the year 1970-71 the Corporation made a gross profit of Rs. 17.07 crores

which, after providing for depreciation (Rs. 11.82 crores) and interest (Rs. 3.58 crores), resulted in a net profit of Rs. 1.67 crores. The turnover of the Corporation has increased to about Rs. 78 crores as against Rs. 66 crores during the previous year. Against an Authorised Capital of Rs. 200 crores, the Corporation's paid up capital stood at Rs. 115.55 crores. The production of nitrogeneous and phosphatic fertilizers in the year 1970-71 are given as:

	Prodn. during 1970-71	Prodn. during Previous Year
Nangal	53,926 tonnes N	79,765 tonnes N
Gorakhpur	67,752 ,, ,,	72,710 ,, ,,
Trombay	57,646 ,, ,,	48,012 ,, ,,
	24,145 ,, P_2O_5	16,988 ,, P_2O_5
Sindri	84,474 ,,	87,306 ,,
Namrup	27,659 ,,	25,821 ,,

Production in Nangal and Gorakhpur decreased because of drastic power cut in the former and power interruptions in the latter. It is anticipated that production in Trombay will improve further. The initial teething troubles at Namrup are being got over; but this plant, because of its low capacity and locational disadvantage, may not significantly improve in profitability till the proposed expansion has been completed. In the case of Sindri Unit, which is an old plant, problems peculiar to ageing continue. The three units of F.C.I. at Nangal, Gorakhpur and Trombay along with P & D Division made a profit of Rs. 4.69 crores. However Sindri and Namrup units have together made a loss of Rs. 3.02 crores.

Increase in the inputs such as electricity rate, naphtha prices, freight, labour cost etc. without a corresponding increase in the sale price of fertilizers have adversely affected the profits of the corporation. The corporation paid an amount of Rs. 5 crores as excise duly on finished products during the year. During the year the corporation had seven major projects under construction. These are Durgapur, Barauni, Rationalization project at Sindri, Namrup expansion, Ramagundam, Talcher and Trombay expansion. This task which is expected to cost approximately Rs. 450-500 crores over a period of approximately 4/5 years, is being carried out entirely by the Planning and Development Division of the Corporation. Durgapur plant is expected to go in stream in the end of 1971 and the projects at Barauni and Namrup are expected to be commissioned by the end of 1972.

Coal based plants at Talcher and Ramagundam to be constructed do not involve recurring foreign exchange in the use of raw materials. Apart from this, the development of coal mines catering to these projects will generate additional employment potential in the coal mining industry to the extent of about 3000 persons in each area. The Planning and Development Division at Sindri continues to play its important role in research and development, planning, designing and engineering, procurement of plants for all the major projects in hand, as well as some of the minor projects forming part of the diversification schemes of the units. Planning of new projects at Haldia, Nangal Expansion, capacity stabilization schemes for Gorakhpur and Trombay, Sindri Modernization and Paradip have also been undertaken.

Design of a private plant to manufacture Sodium Nitrite and Sodium Nitrate based on our know-how has been undertaken by the P & D Divn. F.C.I. is probably the only organization in India which is capable of catering to its own demand for complete design, and engineering services including indigenous process know-how and also making it available to other organizations.

The corporation has established an efficient marketing system to sell the products and there is plan for further expansion. The Eastern Marketing Zone catering to the units in the eastern section has at present 1,000 dealers and 5000 retailers.

Agriculture Insurance

Modern science and technology though helped to eliminate or reduce many risks and uncertainties in agriculture yet even the most developed countries cannot entirely tame nature in order to fully protect farming against large scale loss due to lack of moisture and drought, excess moisture and floods, frost, hail, storms, fire, pests and diseases. Professor Thomson estimated the total crop loss in USA in 1961 was no less than £ 1,197 million due to adverse weather conditions. In the USA lack of moisture or drought is responsible for about 40 per cent of crop losses. In Ceylon it accounts for more than 50 per cent of crop losses and it is a major factor of crop loss in India. Natural hazards are minimized by modern scientific and engineering methods but then new dangers are created. Farm mechanization, the use of pesticides and the risk of contamination, construction of huge dams etc., which though are beneficial invite further risk. The usual classification of social hazards to farming are (a) fire, (b) theft; (c) embezzlement; (d) strikes; (e) war and civil disorder, etc.; (f) changes in social structure and (g) technological changes. The more dynamic and progressive a society, the greater the social hazards. The third major group of risks in farming is of an economic nature. Essentially, such risks include fluctuations in the price of agricultural products, resulting in loss of income to farmers directly through changes in anticipated demand and/or in the supply situation, or through accidental loss of investments, and directly through illness, which affects working ability. The probability of loss or unexpected depreciation of investments from either natural or social causes is becoming increasingly greater with the progressive capitalization of agriculture. These are development and maintenance risks in agriculture. Development risks arise from the investment of capital and labour in the production of new commodities or in the production of old commodities, for example that in agriculture by extending cultivation to poorer soils and the application of increased inputs. The risks occur because the actual yield may fall short of what was anticipated or the increase in products may not find the necessary market, or the investment had been poorly planned or based on an imperfect appraisal of conditions. In maintenance the risks may be for maintaining the present level of production and distribution. To protect the farmers against the risks crop insurance scheme may be introduced. There are three objectives of the insurance programme as practised in the USA: (a) production of the individual farmer's income against the hazards of crop failure or price collapse; (b) protection of consumers against the shortage of food supplies and (c) assistance to business and employment by providing an even flow of farm supplies and establishing stability of purchasing power. Other countries which have already introduced some form of multirisk insurance are Australia, Brazil, Canada, Czechoslovakia, Greece, Israel, Jamaica, Mauritius, Mexico, Puerto Rico, South Africa, Sweden, USSR, Yogoslavia and

also by Ceylon in a small scale. Developing countries in introducing the crop insurance scheme face certain difficulties. There is a scarcity of reliable data over long term period on crop losses. In these countries farms are very small, scattered and segregated. There is very less demand for insurance among farmers and very few farmers would be able to pay the premia. In these countries there is lack of reliable data on land holding, soil classification, productivity and yield of large areas, which could be used for the initial planning. A further problem of crop insurance in developing countries is the lack of suitable trained personnel particularly at the local or village level to assess the problems of agricultural crop insurance. The inception of crop insurance in the initial stages in developing countries will require financial support from governments. But the capital resources available in these countries are strictly limited. The annual ratio of loss to premium earned may be very high. However, given the necessary effort, and with suitable preparation and also by a process of trial and error it is not impossible to make a beginning in many of them. Crop insurance scheme may bring overall welfare and also may give impetus to the farmers for more growth of production.

With all-risk or multirisk crop insurance operating in a number of countries, and others preparing for, or contemplating its adoption, consideration is being given in interested circles as to whether it is possible to provide certain reinsurance facilities on an international level to national systems of crop insurance. The major benefits of such reinsurance would be: first, a greater and wider spread of risks over space and time as compared to reinsurance limited to an individual country; and second, according to the law of average, the larger the number of insurance contracts, the less the variation between annual and average losses, and consequently the less the uncertainty in the aggregate. International reinsurance would thus be of particular benefit to countries in years of catastrophic loss of major crops.

[*Risks in Agriculture and Insurance Coverage* by P. K. Ray, Monthly Bulletin of Agricultural Economics & Statistics **20** (718) (1973), **1**]

Effect of Green Revolution on Developing Nations

Green revolution has brought spectacular change in agriculture by increased production and can be "an unparalleled catalyst for beneficial change", specially in the developing countries. But to many, the green revolution is unleashing a host of unforeseen economic and social problems. It is being said that only rich farmers are being benefited by the green revolution, whereas for the common and poor farmers it has brought no change in their condition. Our aim should be certainly to produce more but there must be proper distribution of the benefits of the produce among all strata of the people. Mr. J. George Harrar, President of the Rockefeller Foundation, has discussed the green revolution and its results. The green revolution is the phrase generally used to describe the spectacular increases that took place during 1960 and are continuing today in the production of foodgrains in several regions of the world, particularly in India, the Philippines, Ceylon, W. Pakistan and Thailand. While a good many farming practices, such as application of fertilizers, pesticides etc., are involved, the basis of the green revolution is the development of new high-yielding seed varieties from which a farmer can produce three or four times as much grain on the same land. The name Dr. Norman E. Borlang, Nobel prize winner for peace, is very much associated for the development and adoption of improved varieties of wheat. The green revolution had its beginning in Mexico in 1940. During the last 30 years this country by using improved varieties of seed has become not only self-sufficient in food but also exports foodgrains. According to FAO's survey, there are in the developing countries about a billion and a half hungry people every one year and it has been estimated that 10,000 people in the world die of malnutrition every day. The hunger problem may get worse if the present rate of agriculture is not increased. The green revolution has proved that vastly increased production can be achieved. In India in 1967-68, only 18 per cent of the wheat acreage was sown to the new dwarf varieties conceived for the Green Revolution, but these varieties produced 40 per cent of India's total wheat crop. In 1968 the national average Indian wheat yield was 1300 pounds per acre, a 62 per cent increase over the average for 1962-65. In the State of Bihar, where famines have been epidemic for hundreds of years, there are today districts where four-fifths of the wheat grown is of high-yielding varieties and yields per acre have increased from 720 pounds to over 1300 pounds.

Figures for Turkey are impressive. The new varieties have made it possible to increase its rice crop by 34 per cent during the past two years. Phillppines has become self-sufficient in food and rice. More food is needed in world and only by green revolution this is possible.

Specific Criticisms of the Green Revolution

(1) Making rich richer and poor poorer; (2) it is the cause of severe unemployment; (3) it is the primary reason for mass migration from rural to overcrowded cities; (4) oversupplies cause the price fall; (5) it is generating within the developing nations a kind of euphoria that encourages leaders to view their soaring population growth rates with complacency.

Probably the most important criticism is the first. Rich farmers with large landholding can afford to purchase the improved techniques, fertilizers and use improved seeds for more yield. He is more likely to have readier access to the cash or credit he needs to buy necessary inputs. In fact, with his resources the rich farmer can control price of foodgrains. Mr. Harrar argues that common farmers may also learn and get inspiration by seeing the rich farmers adopting improved techniques to grow more.

We are all aware of the economic inequalities, the ancient bitterness among various social groups, the deeprooted prejudices, the political injustices and the religious animosities. And it is a historical fact that the introduction of technological change often has the effect of bringing long dormant social ills to the surface and forcing them into greater public awareness. Green revolution may not be the cause of rural unemployment and displacement of agriculture labourers and share croppers that has taken place for decades and is continuing in villages. Population growth is the primary cause of rural unemployment and migration from rural to urban areas. Green revolution in practice should open more employment opportunities in rural areas. Because of increased yields more hands are required at harvest time. And when double and multiple cropping systems are adopted the need for labour increases proportionately. If it is properly directed the green revolution can create new jobs. There is no Asian grain glut due to green revolution. What does confront us is a maldistribution problem.

Governments should adopt the following measures to overcome the difficulties due to green revolution: (1) To see that loanable funds are made available to small scale farmers at interest rates comparable to those received by the large farmers; (2)

greater effort, through extension and research, to determine where and how the new technologies can best be adapted to small farmer groups; (3) wider, more intensive use of trained extension agents who know the rural people and can encourage and guide the smaller farmers during the entire season; (4) positive policies to assure that in the transition from subsistence to market farming, the labour-intensive characteristics of the traditional production methods are retained; (5) exertion of greater efforts to set up small industrial enterprises, service centres, and trading depots in towns and villages, thus providing more new non-agricultural jobs; (6) improvement of intensive marketing and distribution facilities so that the increased food supplies will reach the people who need them, whether in rural areas or in cities; (7) efforts to assure that the farmer is not penalized for his endeavours to increase production by wide fluctuations in the price he receives for his crop.

Green revolution has shown much larger quantities of food can be produced in the very areas of the world where famines, hunger, malnutrition have been endemic. Green Revolution is having constructive, positive and long term influence in ways other than increasing the quantities of food available.

Fertilizer Assignment for Developing Nations

The major fertilizer producers who attended the second Interregional Fertilizer Symposium (held in Kiev, USSR and New Delhi in September and October 1971) complained that the developing nations could make the sagging prices and lacklustre markets of fertilizers worse if they embarked on large-scale investment in domestic fertilizer units. They could rob the big producers of vital export market. Some of these domestic plants, reason the major manufacturers, will be too large for the local markets. The developing nations will then turn to exports, and in their efforts to get rid of excess production, they will be willing to undercut prices, further eroding price levels all over the world.

However, according to United Nations Industrial Development Organization report, bigf ertilizer producers from industrialized nations have little to worry about. These nations now account for 90 per cent of total fertilizer produciion, this percentage will probably be the same in 1980. Despite any plans for local investment, the developing countries' dependence on imports will actually increase up to 1980; these countries now consume 20 per cent of world production and by 1980 they will rise to 25 per cent. Besides, local production in the developing nations cannot begin to match increasing consumption, and the existing gap between the two will further widen by 1980. Although there will be a world fertilizer surplus of 6-8 million tonnes by 1980, the developing nations will not be better off, because they have big gap between production and consumption. In 1969-70 the gap was 5.3 million tonnes; by 1975-76 this will rise to 7.8 million tonnes and by 1980-81 to 9.1 million tonnes. Among the developing nations, total fertilizer deficit in China (3.1 million tonnes), in India (2.65 million tonnes) and in Pakistan (0.95 million tonnes). if the developing nations are to reach their collective production target of 24.2 million tonnes of fertilizer by 1980, effective planning and a large amount of capital will be needed. Even more money would be required to make these countries self sufficient by that time. According to UN study, China, India, Pakistan, Turkey, UAR, Brazil, Cuba, Indonesia and Vietnam are best markets for export of fertilizers. By 1980, only Indonesia and Cuba will achieve a cut in their fertilizer deficit. One common trend to both industrialized and developing countries is the increase in the consumption of nitrogenous nutrients in relation to phosphate (P_2O_5) and potash. By 1980, the world average will be close to 2 : 1 : 1 ($N : P_2O_5 : K_2O$).

Phosphate rock suppliers are threatened by new sources of supply in other countries. It was suggested that developing countries manufacturing Triple superphosphate should import phosphoric acid and phosphate rock. A smaller phosphoric acid plant will be sufficient for this.

The producers should avoid the pitfall of investing in unnecessarily large ammonia or wet-process phosphoric acid units that would result in large quantities of surplus fertilizer into world markets. These considerations do not apply to a country like India, which according to UNIDO study will need 4.2 million tonnes of nitrogen and 1.7 million tonnes of phosphate by 1980. Even if it is true that it is cheaper to import ammonia from the US Gulf coast as per TVA estimate than to make it in India, this country would still profit by embarking on ammonia manufacturing. The importation of 150,000 tonnes/year of nitrogen costs India £ 27 million, a local plant of this capacity can be built for £ 65 million. Of this total the foreign exchange elements i.e., goods, equipment, design services amounting to £ 25 million is spent only once. Proponents of the intermediate industrial option point out that while India can absorb several ammonia and phosphoric acid units of minimum economic size, it is the exception among developing countries rather than the rule.

[Peter Ellwood, *European Editor*, *Chemical Engng*., Dec. 13, 1971, p. 44B]

Replacement of Sulphuric Acid by Hydrochloric for Steel Pickling

In India all steel pickling is done with sulphuric acid, manufactured from imported sulphur. The consumption of sulphuric acid for this purpose is estimated at 48,000 tonnes during 1970-71. The National Metallurgical Laboratory, Jamshedpur have studied the use of hydrochloric acid for pickling.

In India about 25 per cent of steel is pickled by a continuous process while 75 per cent batchwise; the former requires 3 kg per te of net sulphuric acid of steel pickled (with recovery of free acid), while the latter requires 15-17 per kg of 93 per cent acid per te. Assuming these figures and the prices of sulphuric and hydrochloric acids to be Rs. 350 and Rs. 450 per te respectively, it would be seen that hydrochloric acid process will be more costly.

Studies at NML, Jamshedpur have shown that pickling time for complete removal of scale in 14 per cent hydrochloric acid is 1 min. 38 sec. at 46°C while for 17.8 per cent sulphuric acid it is 8 min. At higher temperature although the scale removal is faster and the surfaces brighter and smoother, the acid fumes are too much.

The results on pickling time for hot-rolled steel strip (11 SWG) in hydrochloric acid, containing 2.5, 4.5 and 6.5 per cent iron 45, 60 and 70°C, show that increase in the iron concentration has little effect on the pickling time. This means that unlike sulphuric acid solutions, iron build-up in the pickling bath does not seriously decrease the pickling rates. However, the vapour pressure of hydrochloric acid increases with iron as also with temperature and acid concentration. Higher temperatures and concentrations are necessary for continuous pickling. Quality pickling has been achieved with 31.5 per hydrochloric acid at lime speeds of about 225 m/min. (740 fpm/and speeds exceeding even 305 m/min (100 fpm) can be achieved on horizontal picklers using higher concentration and temper-

atures. An aftertreatment with 2 per cent caustic soda solution is necessary.

The largest proportion of steel is pickled in the form of strip and the two new techniques developed to utilize the advances in pickling and regeneration of pickle liquor are tower and push picklers. The authors have given a scheme of accomplishing the conversion of the existing picklers to hydrochloric acid pickling.

[*NML Tech. J.*, **12** (4) (1970), 87]

New Process for Urea-based Compound Fertilizer

Mitsui Toatsu Chemicals Inc. has developed a new process for the manufacture of compound fertilizers based on urea. The development of the Melt Oil Cooling (MOC) process, as it is called, started in 1964, and the company has just completed evaluation studies of the engineering and operating data from a 500 kg. p.h. pilot plant.

The new process is based on the dispersion of a viscous hot melt of urea, phosphate and potash salt suspension into homogeneously sized droplets. These are then cooled in an appropriate cooling oil to produce solidified prills. A special feature of the MOC process is the use of an oil prilling tank both for cooling and prilling; this eliminates the large and expensive rotary dryer and cooler which are necessary with the conventional processes. As a result, battery limit plant investment costs can be reduced by 20-30 per cent depending on the raw materials used. Utility and labour costs are also diminished since the recycle ratio of the MOC process is low—0.18 per unit of product. Instrumentation simplifies plant operation and the use of oil as coolant results in less dust and fume evolution, as well as in less noise.

The raw materials required for the MOC process are urea, ammonia, phosphoric acid or monoammonium phosphate, and potash salt; no product binding agent is necessary.

In contrast to the irregularly-shaped granules formed by conventional processes, those produced by the MOC process are spherical and free-flowing, with a greater degree of hardness (up to 5 kg. or 11 lb.) and a lower water content (0.5-0.8% by weight). The residual oil in the granules amounts to approximately 0.6% by weight and this helps to prevent caking problems.

Typical grades of urea-based compound fertilizers manufactured by the MOC process of Mitsui Toatsu are 18-18-18, 17-21-17, 28-28-0, 25-30-0 and 25-0-25. Patents relating to this new route have been applied for in 21 countries, throughout the world and some have already been issued.

[*Nitrogen*, No. 72, July-August (1971), 35]

News in Brief

World Science Information System

An Inter-governmental Conference for the establishment of a World Science Information System (UNISIST) organized by Unesco was held at Paris during October 4-9, 1971. Attended by delegates representing 83 member and affiliated states, the conference accepted the recommendations made by Unesco/International Council of Scientific Unions Central Committee for the establishment of UNISIST comprising a flexible network of the existing and future information services which will be multilingual. UNISIST will embrace all fundamental sciences, applied sciences and technology. The conference recommended the constitution of a steering committee of 18-23 members charged with the responsibility of implementing the UNISIST programme and of revising the priorities of the programme within the framework of the long-term plan of action. Director-General, Unesco was called upon to make adequate budgetary provision to enable Unesco to play its leading role in the rapid establishment of the first stages of UNISIST, taking into account the needs of the developing countries.

[*CSIR News*, **21** (23) (1971), 177]

National Committee on Science and Technology

The National Committee on Science and Technology, constituted by the Government of India, was inaugurated by Sri V. V. Giri, President of India on November 16, 1971 in New Delhi. Its main task will be to help evolve a national policy for the promotion of science and technology and to advise the Government on the following: (i) Preparation, evaluation and updating of national, scientific and technological plans —both 5 year and perspective plans—in close cooperation with the Planning Commission; these plans would be intimately related in terms of relative priorities and the allocation resources to the national planes; (ii) pattern and mode of development of science and technology, including measures for correcting imbalances; (iii) attainment of scientific and technological self-reliance and the full utilization of the nation's scientific, technological and industrial resources; (iv) commitment regarding education and manpower development indicated in the scientific policy resolution; (v) coordination, co-operation and communication between Government and semi- or non-Government scientific institutions; (vi) international scientific and technological matters including co-operation; (vii) periodical discussion of science and technology policy issues; and (viii) any other matter.

NCST will make its recommendations to the Science and Technology Committee of the Cabinet through the Minister of Planning and Science and Technology. Its major task would be the preparation of Science and Technology Plan as a part of the National Plan.

The members of NCST include: Dr. Hari Narain, Dr. A. R. Kindwai, Dr. A. K. Malhotra, Dr. V. Ramalingaswami, Prof. C. N. R. Rao, Dr. R. Ramanna, Sri M. M. Suri, Dr. M. S. Swaminathan, Dr. R. V. Tahamankar and Dr. B. D. Tilak.

[*CSIR News*, **21** (23) (1971), 177]

Pesticide

Gujarat Agro-Industrial Corporation is setting up a factory at Godhra for the manufacture of lindane, a basic chemical for pesticides. The project is for production of 7.5 tonnes of lindane per year. The know-how has been released to the party by the Central Food Technological Research Institute, Mysore.

[*Inform. News Letter, Indus. Lia. & Exten. Serv., CSIR*, **10** (2) (1971), 27]

Imports Reduction

Inaugurating the annual general meeting of the Indian Chemical Manufacturers' Association, Sri C. Subramaniam, Minister for Planning, Government of India asked the leaders of chemical industry to collaborate with the national committee on science and technology in reducing the country's dependence on external sources for products, equipment and technology. He pointed out that about Rs. 60-70 crores of fertilizer was being imported every year. This could be brought down to Rs. 25-40 crores by fully utilizing available capacity and producing 200,000-300,000 tonnes of nitrogen.

Indian Institute of Petroleum

The research and development programme of IIP Dehra Dun includes work on crudes, catalysis, catalytic reformation processes, etc.

Evaluation of Crudes: This is a continuation of previous work for collecting basic data on the characteristics of crudes to assess the product pattern of fuels, lubricants, petrochemical feedstocks and speciality products. Problems in this area originating from the ONGC, IOC and the Indian Petroleum Corporation Ltd., and Union Ministry of Petroleum and Chemicals are of prime interest to the public sector refineries and other extrepreeus using petroleum products. Evaluation of crudes from Darius, Rostam, Aghajari and Morgan (Middle East) is also being carried out.

Catalysis: A study of the mechanism of catalysis for use in petrochemical and refining industries is in progress. Facilities for investigation of surface acidity, true and particle densities, adsorption and surface area measurements, pore size distribution have been developed. Processes for the production and evaluation of specific catalyst and catalyst supports are being developed.

Protein from Petroleum: After successful laboratory trials, a pilot plant for production of 15-20 kg/batch of protein concentrate using gas oil as the feedstock has been set up.

[*CSIR News*, **22** (1) (1972), 1]

Tata's Fertilizer Project

Tata Chemicals Ltd. has started taking active steps to implement the fertilizer project at Mithapur as the project has been cleared by the Government of India. Its cost is now estimated at about Rs. 44 crores including foreign exchange component of about 50 per cent. The Government

is understood to have accepted the company's view that the manufacture of the phosphatic fertilizers could be deferred till the company is able to evolve and develop its own technology to manufacture phosphoric acid without imported sulphur. Under the modified scheme the company will produce in the first stage 2.10 lakhs tonnes of ammonia, 2 lakhs tonnes of urea and 1.80 lakh tonnes of ammonium chloride per year.

Coking Coal Mines

The Government of India has constituted a company for 214 coking coal mines, whose management was taken over recently. It will be known as Bharat Coking Coal Ltd., having an authorized capital of Rs. 50 crores with its registered office located at Dhanbad (Bihar).

Corrosion in Phosphoric Acid Plants

In a paper presented at a recent symposium of the Fertilizer Society on plant maintenance problems, D. L. Clarke and R. C. Williamson cited the case of agitators in a phosphate rock/sulphuric acid reaction vessel which although made of type 316 stainless steel, dissolved at the rate of 80 mm/a. They found that once an agitator gained a history of corrosion it remained active even if scraped and cleaned. And this active agitator could trigger off corrosion in a passive agitator. To overcome this exceptionally high corrosion rate the authors suggest two controls. Firstly, a monitoring device should be incorporated to measure the rate of corrosion. This can be a simple set-up consisting of silver wire reference electrode, a voltmeter and a chart recorder. Then the electro-chemical potential of a specimen of metal from the plant can be indicated against a reference electrode when immersed in the reaction liquor. This simple measurement can show if the plant is corroding or not, provided a potential-corrosion rate curve (obtained from a potential-current curve) has been worked out for the plant metal electrode.

The second way of controlling corrosion rate is to add a trace quantity of oxidizing agent to the liquor, this is known to reduce corrosion rates of stainless steels in acid solution. The authors carried out experiments using nitric acid as the oxidizing agent, but this particular inhibitor is not recommended, as it could possibly turn into a corrosive agent at certain concentrations. It can also affect rubber-lined plant downstream from the reactor. Instead they recommend copper sulphate, where tests showed that it quickly changes the agitator to passive state. Ever after the copper sulphate passed out of the reactor, corrosion did not occur, and it was some weeks before further quantities of copper sulphate had to be added.

[*Chem. and Process Engng.*, **55** (7) (1971), 5]

Sulphur for Coating Fertilizers

In using a spray of molten sulphur to produce a coating on fertilizer granules, the former solidifies forming a semi-permeable shell having low impact strength. Unless the surface is covered completely with sulphur, the substrate will dissolve quickly in water; in fact, a heavy coating is required to obtain a suitable barrier. This problem is solved by first dusting the uncoated granules with 0.2-3.0 per cent of a powdered material, such as carbon black, zinc borate, carbonate, chromate or sulphide, magnesium hydroxide or silicate and other compounds. The powder coating decreased the contact angle between the granule and the molten sulphur which makes possible the production of satisfactory coatings of sulphur using 5-10 per cent sulphur. Such a coating is used in commercial granular urea 29-14-0, 20-10-10 and 18-46-0.

[P. S. Fleming, *US Pat No.* 3,576,613 (April 27, 1971); *FAI Abst. Serv.*, **10** (9) (1971), 5]

Indigenous Iron For Hydrogen Production

Iron ore used in the process of making industrial hydrogen is known as sphathic iron ore, which is being imported from Spain. While carrying out geological investigations on the lignite deposits of Panandhro area (Kutch district, Gujarat), Central Fuel Research Institute came across a siderite deposit (iron carbonate), which is similar in properties to the Spainsh ore. It can be used for the generation of hydrogen by steam-iron process. A total reserve of 4.6 million tonnes has been estimated in the above area and a similar quantity is anticipated in the adjoining Akrimota field.

[*CSIR News*, **21** (15) (1971), 115]

New Rice Insecticide

Entomologists of the International Rice Research Institute, Manila have found a new insecticide—Carbofuran—which can effectively control rice stem borers, green leaf hoppers, brown plant-hoppers and leaf-feeding insects. This insecticide is highly soluble in water even at low temperature and has been found to be more effective than either Diazinon or Lindane and that it can control more species of insect pests than either of the two insecticides. It can be applied as a leaf spray or directly to the paddy water.

[*Press Gleanings, FCI Ltd., New Delhi,* **1** (4) (1971), 7]

Urea as Contraceptive

Urea is being used for the first time in the medical history for producing a soluble contraceptive costing not more than a paisa each at the Central Drug Research Institute, Lucknow. The new contraceptive, named as Cent Square, has already been approved by the Central Drug Controller for clinical trials, and it has already been tested in Delhi and Lucknow. CDRI has already filed a patent application.

[*Press Gleanings, FCI Ltd., New Delhi,* **1** (4) (1971), 4]

New Advisory Body on Science and Technology

Government of India has decided to establish a National Committee on Science and Technology (NCST) in place of the Committee on Science and Technology, which ceased to exist from August 1971. This committee, under the Department of Science and Technology, will advise the Government and the Planning Commission about the priorities that have to be followed for research and development particularly with a view to utilizing the resources within the country. Sri C. Subramaniam, Planning Minister, who will also look after NCST, told reporters on August 27 that the new body would help in the efficient execution of the socio-economic plan. Being a high level body, NCST will have a full-time chairman, who would necessarily be a scientist.

Korba and Haldia Fertilizer Projects

Sri P. C. Sethi, Minister for Petroleum and Chemicals, Government of India, announced recently that the Finance Ministry has given its approval for such major fertilizer projects as Korba and Haldia and work on these will begin soon. Haldia would involve an investment of Rs. 85 crores and Korba of Rs. 15 crores in the first stage to be completed in the Fourth Plan period. Korba would eventually be expanded to produce 229,000 tonnes of nitrogen at a total investment of Rs. 95 crores.

Ammonia Accidents—Major Blindness Cause

Accidental exposure of ammonia fertilizers to a person's eyes is one of the major

causes of blindness being reported by univ. Hospitals in Iowa, says C. W. Bockhop, Iowa State Univ. Safety Specialist.

The major causes of accidental exposure appear to be hoses coming loose from application equipment or bursting during applications of anhydrous ammonia.

Anyone using ammonia fertilizer products should heed the following suggestions given by Bockhop: (1) Wear protective goggles or face shield and gloves; (2) Understand thoroughly how to operate a piece of equipment before you attempt to do so. All hose fittings and connections are to be checked daily that they do not leak; and (3) Water is the best emergency first aid treatment from ammonia solutions burns. If the burns are extensive, the victim should be immersed in the tank. Exposed areas should be flushed or irrigated for at least 15 minutes with water. Never apply salves or ointments to ammonia burns unless directed to do so by a physician. All contaminated clothing should be removed as soon as possible. Clothing may be frozen to the skin due to freezing action of anhydrous ammonia. When this happens, thaw with water before attempting to remove clothing.

A victim should be kept warm and taken to a physician after the exposed area has been flushed with water. The doctor should be told that ammonia caused the injury.

[*Crops and Soils*, **23** (8), (1971) 19]

Patents*

Danger Aspects of Fertilizers Containing Ammonium Nitrate The M. Groothuizen, E. W. Lindeijer, and H. J. Pasman (Technol. Lab., Nat. Def. Res. Org. TNO, Rijswijk, Neth). Stikstof, No. 14, 31 pp. (1970).

Fertilizers containing a large amount of NH_4NO_3 may deflagrate as a result of localized heating or by self-heating, with large quantities of toxic gases such as HCl, CI_2, NO_2, N_2O, and NOCI being evolved. The heat development in a fertilizer fire is mainly caused by the reaction between NO_3 as the oxidizing agent and NH_4^+ as the reducing agent. Detonation sensitivity has to be considered when storing and transporting such fertilizers. Thermal decomposition of NH_4NO_3 and gas-chromatographic analysis of gaseous decomposition products are discussed.

[*Fertil. Abstr.*, **4** (2) (1971), 27]

*These patents have been reproduced from *Fertilizer Abstracts*, published by the National Fertilizer Development Centre, Tennessee Valley Authority, Muscle Shoals, Alabama (USA), with kind permission of the Editor of FA—Editor.

Benefication of Phosphate Ores Containing Calcite and Quartz G. K. Korpi and C. S. Wiedemann (to International Minerals and Chemical Corp.). U.S. 3,534,854, Oct. 20, 1970, Appl. Nov. 20, 1967; 4 pp.

The ore, ground and deslimed in the usual way for preparing feed for froth flotation, is subjected to two successive anionic flotations at pH 10-12, and 6-7.5, respectively. The first flotation removes calcite in the floats; the second produces an apatite-rich concentrate as the float. Suitable anionic flotation reagents include fatty acids or their soaps. The same reagents are used in both flotations; only the pH is changed. In an example, a North Carolina phosphate ore containing 8.2 per cent P_2O_5 and comprised of 36.9 per cent apatite, 11.4 per cent calcite, and 51.8 per cent quartz, was beneficiated to give a concentrate containing 27.8 per cent P_2O_5 with a recovery of 77.5 per cent.

[*Fertile. Abstr.*, **4** (2) (1971,) 29]

The Kellogg-Lopker Phosphoric Acid Process L. E. Bostwick and William Turner (Kellogg International Corp. London. England). Fertilizer Ind. Round Table, Proc. 19th, pp. 5-10 (1969).

A process is described by which phosphate rock is completely reacted with H_2SO_4, and the resulting $CaSO_4.2H_2O$ crystals grow rapidly to such size and shape that separation of product H_3PO_4 is more rapid and complete than with other processes. Two vessels, vertically offset, are interconnected to provide a recirculating flow path. Phosphate rock and recycled phosphoric acid are introduced into the dissolved (lower vessel), maintained at atmospheric pressure, and reacted with a variety-fed slurry from the evaporator (upper vessel), maintained at reduced pressure. The slurry enters the dissolver tangentially, imparting a swirling motion. The resulting slurry is pumped into the evaporator, entering tangentially, and sulfuric acid is introduced. Product slurry is withdrawn for filtration at either the inlet or the outlet to the evaporator. Approximately half of the CO_2 and F_2 is released in the dissolver, reducing the load on the vacuum system. The process operates with constant recirculation ratio, resulting in plug-flow and no back-mixing. Changes in Ca^{2+} and SO_4^{2-} concentrations are very small, controllable, predictable, and are separated in time as well as in space. Phosphoric acid produced per square ft. of effective filtration area is considerably greater than from a conventional process using the same rock.

[*Fertil. Abstr*, **4** (2) (1971), 30]

Ion Exchange Resin Purification of Wet Process Phosphoric Acid J. T. Minor, S. J. Lokken, and W. H. Kegler (Continental Oil Co., Ponca City, Okla.). Fert. Solutions 14 (6), 62-70 (Nov-Dec. 1970).

Pilot plant tests are described in which cation exchange resin in the H form is used to remove K and Mg from filter acid. By choosing the appropriate amount of resin and the number of passes, filter acid can be purified sufficiently to avoid post precipitation when the acid is concentrated to 54 per cent or when made into base solutions such as 10-34-0. For example, in two passes Mg was decreased from 0.11 to 0.036 per cent; K was decreased from 0.013 to 0.008 per cent; and Ca was decreased from 0.077 to 0.031 per cent. Iron and Al were not decreased significantly.

[*Fertil. Abstr*, **4** (2) (1971,]

The Hemihydrate Process and the Gypsum Challenge R. M. Daniel (Day and Zimmerman, Inc., Philadelphia, Penn.). Fertilizer Ind. Round Table. Proc. 19th, pp. 11-15 (1969).

The problem of the fertilizer industry in developing markets for byproduct gypsum is the gypsum challenge. Gypsum produced by the Japanese developed hemihydrate-process, also referred to as the hemihydrate-dihydrate process, is more competitive with natural gypsum than that produced by the dihydrate process because it contains less residual P_2O_5 and other impurities that degrade the product. The hemihydrate process is a technique for manufacturing wet process H_3PO_4 by digesting phosphate rock at a temperature which causes the calcium sulfate to form as $CaSO_4$ $2H_2O$. In a subsequent step at a lower temperature, the hemihydrate takes on additional water of crystallization to form $CASO_4.2H_2O$ which is separated from H_3PO_4 by filtration. Improved economy is due to reduced requirements for phosphate rock, H_2SO_4, electricity, and maintenance per unit of P_2O_5 produced.

[*Fert. Abstracts*, **4** (2) (1971), 31]

Preparation of Water-Soluble Nitrogen-Phosphate Fertilizers Ugine Kuhlmann S.A. Brit. 1,182,395, May 22, 1968, Fr. Appl. May 22, 1967. J. Sci. Food Agr. 21 (8), ii 50 (Aug. 1971).

Phosphoric acid, preparation by the wet process and containing P_2O_5 30-55 wt per

cent and various impurities including H_2SiF_6, is first defluorosilicated by addition of an equal molecular amount (referred to H_2SiF_6) of a Na salt (Na_2CO_3) to yield insoluble Na_2SiF_6, which is filtered off, and a solution of defluorosilicated H_3PO_4 which is ammoniated to yield an aqueous solution, pH 5-6. This is dried to give an anhydrous ammoniated phosphate which is treated with 0.2-0.9 moles of urea/mole of P_2O_5 for 15-70 min at 130-170° to produce a completely water-soluble NP fertilizer.

[*Fertil. Abstr.*, **4** (2) (1971), 32]

Ammonia Synthesis, Friedrich Uhde G.m.b.H. Brit. 1,189,376, Apr. 22, 1970, Swiss Appl. Apr. 25, 1966; 6pp.

In a process for NH_3 synthesis, the reaction gas is divided into two streams which are recycled to the catalytic reactor. One of the streams is heated to the priming temperature and passed to the topmost layer of catalyst. The other stream is preheated by heat exchange with the reacted gas after it has passed through the apparatus; it is then fed to the reactor directly into the catalyst bed and/or between the layers of catalyst. This method increases the life of the catalyst, and decreases heat consumption and heat exchanger size.

[*Fertil. Abstrs*, **4** (3) (1911), 53]

Injection of Liquid Ammonia into Soil R. L. Every and R. M. Tillman (to Continental Oil Co.). U.S. 3,538,867, Nov. 10, 1970, Appl. Feb. 14, 1968; 1 p.

The jet method of injecting liquid NH_3 into agricultural soil consists of directing a high pressure stream, or discrete slugs, toward the soil. A major advantage of this method, compared with the older method of cutting a deep slit in the soil, metering NH_3 into the slit, and pressing the slit closed by wheels or shoes, is that very little disturbance of the soil surface is required (Cf. U.S. 2,988,025). In using the jet method, greater penetration into the soil is obtained by dissolving at least 5 per cent urea in the NH_3.

[*Fertl. Abstrs.*, **4** (3) (1971), 53]

Urea Production in Combination With Ammonia Synthesis Stamicarb on N.V. Brit. 1,207,923, Oct. 7, 1970, Appl. Neth Mar. 16 1968; 5 pp.

Ammonium carbamate—containing urea solution from the urea synthesis zone—is subjected to a two-stage stripping treatment. Both stages are operated at substantially equal pressures. The treatment in the primary stage is carried out with the initial gas containing H and CO_2. In the secondary stage the gas is substantially free of NH_3 and CO_2 and contains one or more of the components needed for NH_3 synthesis. Stripping gases suitable for use in the secondary stage include H, N, and H-containing gas obtained by removing NH_3 and CO_2 from the gases withdrawn from the primary stripping stage. The stripping treatments are preferably carried out at urea synthesis pressure, or at least 300 atmospheres. The method avoids deposition of solid ammonium carbonate in compressors, and the use of corrosion-resistant compressors.

[*Fertil. Abstrs*, **4** (3) (1971), 53]

Urea Production Combination with Ammonia Synthesis Stamicarbon N. V. Brit. 1,207, 924, Oct. 7, 1970, Appl. Neth Mar. 16, 1968; 5 pp.

Synthesis gas comprised of H and CO_2, and possibly N, together with CO as a contaminant, is fed to an $NH_4NH_2CO_2$-forming zone which is part of a urea synthesis zone. The effluent gas, freed from CO_2, is fed to an NH_3—synthesis zone. The NH_3 is fed to the $NH_4NH_2CO_2$-forming zone. Oxygen (air) is added to the fresh synthesis gas, based on the amount of CO in the synthesis gas. The effluent gas from the $NH_4NH_2CO_2$-forming zone is treated to catalytically oxidize the CO. The resulting CO_2 is removed from the gas by washing with an ammoniacal solution, and the wash liquor is recycled to the $NH_4NH_2CO_2$-forming zone.

[*Fertil. Abstrs*, **4** (3) (1971), 53]

Defluorination of Phosphoric Acid W. E. Rushton (to Whiting Corp.). U.S. 3,544, 269, Dec. 1, 1970, Appl. Feb. 27, 1967; 7 pp.

Wet-process H_3PO_4 is defluorinated by contact with superheated steam at reduced pressure. The acid can be contacted with the steam in a scrubbing column provided with deflector plates in which the acid is fed at the top and the steam is fed at the base. Or defluorination can be carried out concurrently with acidulation of the phosphate rock in a forced circulation vacuum evaporator-acidulator (Cf. FA 1, 975). In the latter case the steam is introduced at the base of a draft tube having upward flow. In either case the temperature and vacuum are regulated so that the added steam does not condense in the vessel.

[*Fertil. Abstrs*, **4** (3) (1971), 54]

Granular Fertilizers Eiji Otsuka et al (to Mitsui Toatsu Chemicals, Inc.). U.S. 3,539,326, Nov. 10, 1970, Appl. Japan Aprl. 1, 1966; 8. pp.

In preparing granular NP or NPK fertilizers by prilling a melt prepared from dry-mixed raw materials the mixture passes through a sludgy stage where heat transfer is low and decomposition is probable. A method is described for eliminating this problem; a melt is prepared from aqueous urea and/or NH_4NO_3, and the other constitutents such as $NH_4H_2PO_4$ and KCI are preheated in dry form and added to the melt. The resulting mixture is then fed to a prilling tower. For example, 1.2 kg $NH_4H_2PO_4$ and 1.0 kg KCI, both preheated to 120°, were added to 1.5 kg molten urea at 150-170°. The resulting mixture was then vigorously stirred at 130°. In 6 min a fluid suspension was obtained having a viscosity of 500-1000 centipoise. When stirring was continued the viscosity increased, and in 5 min the fluidity was lost and the mixture became impossible to prill.

[*Fertil. Abstrs*, **4** (3) (1971), 56]

Anticaking Treatment for Granular Fertilizers. Imperial Chemical Industries Ltd. (by James Jack et al). Brit. 1,189,335, Apr. 22, 1970, Appl. Apr. 24, 1967; 14 pp.

Certain types of silanes or siloxanes do not require heat treatment to improve the durability and anticaking properties of granular hygroscopic fertilizer materials such as urea and NH_4NO_3. Examples include alkyltriethoxy silanes in which the R group is a straight-chain alkyl group containing 8-18 C atoms, and organopolysiloxanes such as cyclic or linear methyl hydrogen siloxanes. These compounds can be mixed with finely-ground inert material such as clay which is then applied to oil-coated granules of the fertilizer. Or they can be applied with the oil coating and then mixed with the dusting agent.

[*Fertil. Abstrs,* **4** (3) 1971). 56]

Influence of Moisture on the Structure and Quality of NH_4NO_3 Prills. Christer Sjolin (Agr. Inst., Dublin, Ireland). J. Agr. Food Chem. 19 (1), 83-95 (Jan. Feb. 1971).

A study was made of high density NH_4NO_3 prills with additives of 1 wt per cent $Al_2(SO_4)_3$ and 2 wt per cent $Mg(NO_3)_2$. Prills with no additive were used as reference material. The purpose was to determine the effect of the additives on the structure of prills and the reason for resultant high-quality and good dimensional

stability. The methods used were scanning-electron microscopy, optical microscopy, X-ray diffractography, electron micro-analysis, and high-energy electron diffractography. The results show that the additives are not homogeneously located in the prills. The $Mg(NO_3)_2$ additive is located in veins between the crystallites and contains 2-6 moles of water of crystallization. The $Al_2(SO_4)_3$ additive is located in small aggregates, diameter 1 to 10, with the formula $Al_2(SO_4)_3(NH_4)_2(OH)_2(H_2O)_{6-10}$. The better dimensional stability is principally due to the additive taking up moisture from the surrounding NH_4NO_3 bulk which results in a water-content low enough (0.01 per cent) to prevent the phase transition IV III at 32°. The phase transitions were studied with x-ray diffractography.

[*Fertil. Abst*., **4** (4) (1971), 79]

Inhibiting Biuret Formation in Preparing Urea-Based Fertilizers Fisons Fertilizers Ltd., (by D. J. Chapman). Brit. 1,218,174, Jan. 6, 1971, Appl. Feb. 3, 1967; 3 pp.

Ammonium phosphate is added to a suspension of an ammonium salt and/or K salt in molten urea held at a temperature no greater than 125°, followed by granulating the mixture. For example, 35 parts powdered KCI was added to 100 parts molten urea at 133°. The resulting slurry was allowed to cool to 117°, and 33 parts powdered $NH_4H_2PO_4$ was added. There was no evolution of CO_2 and NH_3 from the slurry. In contrast to this test, vigorous frothing and evolution of CO_2 and NH_3 occurred when 33 parts NH_4H_2 PO_4 was added to 100 parts molten urea at 133°.

[*Fertil. Abstrts*., **4** (No. 4), April 1971, 80]

Inhibiting Biuret Formation in Preparing Urea-Potassium Fertilizers. Fisons Fertilizers Ltd. (by D. J. Chapman). Brit. 1,218, 176, Jan. 6, 1971, Appl. Feb. 22, 1967; 2 pp.

A molten mixture of a K salt and urea allows the use of lower temperatures than required for a urea melt, and thereby decreases biuret formation in melt preparation of N-K fertilizers. For example, a eutectic mixture comprised of 12.2 parts KCI and 100 parts urea was molten at 122° compared with 132.7° for urea alone. Urea at 20 parts/hr and KCI at 2.45 parts/hr ware added to the eutectic melt, and 22.45 parts/hr mixture was withdrawn and prilled. The product contained only 0.5 per cent biuret.

[*Fertilizer Abstracts* **4** (No. 4), (1971), 80]

Phosphoric Acid. G. E. G. Wilkinson and T. T. Houston (to Tennessee Corp.). U.S. 3,554,696, Jan. 12, 1971, Appl. May 6, 1968; 5 pp.

In the manufacture of wet-process H_3PO_4, the Fe and Al phosphates that precipitate during the concentration step are separated and recycled to the acidulation step. The precipitate dissolves in the acidulation mixture, and the P_2O_5 is largely recovered in the product H_3PO_4. There is no significant increase in the P_2O_5 lost in the by-product gypsum. Furhermore the level of Fe and Al does not exceed a tolerable equilibrium in the circuit. The method recovers the P_2O_5 in the precipitate without the need for using it to produce co-products such as mixed fertilizers or triple superphosphate.

[*Fertil. Abst.* **4** (No. 4) (1971), 81]

Solid and Liquid Ammonium Polyphosphate Fertilizers. W. P. Moore, J. E. Sansing, and Joseph Novotny (to Allied Chemical Corp.). U.S. 3,554,728, Jan. 12, 1971, Appl. Aug. 5, 1968; 4 pp.

Crude wet-process H_3PO_4 is concentrated to 50-54 per cent P_2O_5 and allowed to stand 3 days at 60°. The resulting acidic sludge is separated, and the clarified acid is dehydrated to form superphosphoric acid containing 72 per cent P_2O_5. The superphosphoric acid is then reacted with aqua ammonia at 90° and 15 psig to give a N: P_2O_5 ratio of 0.41:1 and a pH of 8.5. The resulting over-ammoniated superphosphoric solution is cooled to 60° and allowed to stand for 24 hr at 60°. The resulting alkaline precipitate is separated by centrifuging. The clarified solution, containing 34.3 per cent P_2O_5 (58 per cent as polyphosphate) and 17.4 per cent NH_3, is treated to strip out the excess NH_3 and produce an ammonium polyphosphate fertilizer solution having a pH of 6.2 and containing P_2O_5 33.7, NH_3 12.2, and MgO 0.07 per cent. The acidic sludge and the alkaline sludge from the foregoing operations are fed to a rotary drum reactor-granulator, together with recycled product heated to 90° to maintain the temperature at 55-65°. The recycle ratio is 5:1. The solid product consists of non-hygroscopic ammonium polyphosphate fertilizer containing P_2O_5 55.8, NH_3 16.84,, MgO 3.96, H_2SO_4 4.36, Al_2O_3 2.27, and Fe_2O_3 3.69 per cent. The citrate solubility of the P_2O_5 is 99.5 per cent and the water solubility is 63 per cent. Conversion of non-orthophosphate to orthophosphate during granulation is about 15 per cent. The process produces a high-analysis liquid fertilizer low in Mg and a high-analysis non-hygroscopic granular fertilizer.

[*Fertl. Abst*., **4** (1971) No. 4) 82]

Evaluation of Phosphorus Nitrogen Compounds as Fertilizers. Z. T. Wakefield, S. E. Allen, J. E. McCullough, R. C. Sheridan, and J. J. Kohler (Tennessee Valley Authority, Muscle Shoals, Ala.), J. Agr. Food Chem, 19-102 (Jan.-Feb. 1971).

Thirty-four P-N compounds were prepared in the laboratory and compared in the greenhouse as high-analysis sources of fertilizer N and P for corn. The compounds included phosphonitrilic derivatives, metaphosphimates, metaphosphates, S-containing compounds, and amido-and imidophosphates. The metaphosphates, amidophosphate thiomidophosphates, and phosphoryl triamide were excellent sources of both N and P, but metaphosphimates were poor sources. Several of the S compounds were toxic in early growth stages, but thereafter were effective sources of plant nutrients. Of the phosphonitrilic derivatives, only phosphonitrilic hexaamide was an effective source of both N and P.

[*Fertil. Absts.* **4** (No. 4) (1971), 83]

Granular Ammonium Nitrate-Phosphate Fertilizer R. E. Alston (to Northwest Nitro Chemicals, Ltd.,). U.S. 3,545,954, Dec. 8, 1970, Appl. Aug. 29, 1967; 3 pp.

A mixture of finely-ground NH_4NO_3 and ammonium phosphate is compacted to form a sheet which is then broken to form coarse flakes or chips. The material is then ground and sized to prepare granules of desired size. Examples describe the preparation of 23-23-0 and 27-14-0 grade of product from NH_4NO_3 and commercial NH_4PO_4 (11-48-0).

[*Fertil. Absts*., **4** (No. 4) (1971), 83]

Separation of Calcium Nitrate from Nitrophosphate Solutions. J. W. Markey and E. C. Comp (to Cities Service Co.). U.S. 3,560,149, Feb. 2, 1971, Appl. Apr. 29, 1968; 12 pp.

Phosphate rock is digested with concentrated (75-85 per cent) HNO_3 to prepare a solution containing H_3PO_4 and $Ca(NO_3)_2$. The solution is then treated with substantially anhydrous HNO_3 whereby most of the $Ca(NO_3)_2$ is precipitated in anhydrous HNO_3 whereby most of the $Ca(NO_3)_2$ is precipitated in anhydrous form. The precipitate is separated, and the solution is distilled to separate the HNO_3 and obtain

H_3PO_4 as product. Optionally the mixture of H_3PO_4 and HNO_3 can be ammoniated to produce N-P fertilizers. The anhydrous $Ca(NO_3)_2$ is specially suited for thermal decomposition to regenerate HNO_3. In an example, phosphate rock containing 30 per cent P_2O_5 and 47 per cent CaO was crushed to −30 mesh. The rock was digested for 1 hr at 240°F. with 80 per cent HNO_3 using 2.74 parts HNO_3/part CaO. the digestion slurry was mixed with two parts 97.2 per cent HNO_3/part original rock causing precipitation of 98 per cent of $Ca(NO_3)_2$. Data are given on the effects of HNO_3 concentration and ratio on extraction of P_2O_5 and precipitation of $Ca(NO_3)_2$.

[*Fertil. Absts.* **4** (No. 4), (1971), 84]

Mixed Fertilizer Granulation. Gulf Oil Corp. Brit. 1,218,166, Jan. 6, 1971, U.S. Appl. May 7, 1968; 5 pp.

Dust emission is a problem in granulation of mixed fertilizers. In the process described, dust emission is reduced by production of granules rather than fines. The process involves (1) mixing H_3PO_4 with recycled fines and oversize to form a slurry; (2) feeding the slurry into a rotary drum along with sized feed solids; (3) feeding a stream of molten NH_4NO_3 at the time; (4) adding NH_3 to react with acidic constituents; (5) recycling 50 to 75 per cent of the hot, moist granules formed in the drum back to the inlet; (6) drying and cooling the remainder of the moist granules; (7) screening to product size; and (8) recycling fines and oversize. It is claimed that the process produces less dust than the usual method.

[*Fertil. Absts.* **4** (1971), 84]

Phosphate Recovery from Sewage Effluent

The latest in a series of processes aimed at reducing the level of phosphates in sewage effluents has been proposed by scientists at the University of Toronto. Based on a reciprocating-flow ion-exchanger, the process is claimed to remove over 99 per cent of the total phosphates present in sewage, ultimately in the form of magnesium ammonium phosphate. The process has yet to be proven on a large scale operation, but a similar ion-exchange plant has been in operation industrially to remove anions other than phosphates.

[*Phosphorus and Potassium,* No. 49, 1970, p. 56]

STATISTICS

TABLE 1—Analysis of Various Rock Phosphates Available for Fertilizer Manufacture

(a) Indigenous—Udaipur Rock phosphate

Analysis	Typical analysis of Jhamar-Kotra (near Udaipur) rockphosphate (with accepted variations)
Phosphorus pentoxide (P_2O_5)	30 to 37 per cent
Calcium oxide (CaO)	40 to 53 ,, ,,
Magnesium oxide (MgO)	0.5 to 2.5 ,, ,,
Silicon oxide (SiO_2)	3 to 8 ,, ,,
Oxide of iron and alumina (R_2O_3)	1.50 to 6 ,, ,,
Calcium fluoride (CaF_2)	0.95 to 3.6 per cent
L.I.O.	1 to 4 per cent

Source: Directorate of Geology and Mines, Government of Rajasthan, Udaipur

(a) Indigenous—Kasipatnam Rock phosphate

Analysis	Typical analysis of Kasipatnam rockphosphate
Total P_2O_5	41.9 per cent
Water soluble (P_2O_5)	0.08 ,, ,,
Iron (Fe)	0.05 ,, ,,
Silica	1.6 ,, ,,
Moisture	0.13 ,, ,,
Chlorine (Cl)	0.07 ,, ,,
Tribasis phosphate of lime	91.56 ,, ,,

(b) Imported

Analysis	Tunisia @ (Gafsa) rock phosphate %	Moroccan rock phosphate @ %	Moroccan rock phosphate @ %	UAR (Safaga) phosphate %	American @ pebble phosphate %	Kossier* Phosphate %	Jordan @ rock phosphate %	Togo* rock phosphate %	Algerian rock* phosphate %	Sengal** rock phosphate %	Analysis
Moisture	2.03	—	1.27	2.50	—	—	1.90	1.50	0.29	0.55	Moisture
Contents on dry basis											Contents dry basis Com
Combined water and organic matter	3.44	1.63	0.81	—	2.83	1.24	—	1.44	—	1.65	bined water and organic matter
Phosphorus pentoxide (P_2O_5)	30.22	35.11	37.21	28.8-29.8	35.29	29.86	32.67	36.85	34.58	37.55	Phosphorus pentoxide (P_2O_5)
Titanium	—	0.205	—	—	—	—	—	—	—	—	Titanium
Sulphur trioxide (SO_3)	2.84	1.4	0.62	2.70	0.56	2.51	1.05	0.40	1.60	0.22	Sulphur trioxide (SO_3)
Carbon dioxide (CO_2)	5.73	4.12	2.64	6.50	2.99	6.09	5.20	1.50	1.25	1.68	Carbon dioxide (CO_2)
Siliceous	2.37	—	0.97	3.51	3.95	4.98	3.55	2.99	2.35	2.98	Siliceous
Oxide of alumina (Al_2O_3)	0.65	0.45	0.39	—	1.00	1.50	0.35	1.00	0.45	1.39	Oxide of alumina (Al_2O_3)
Oxide of iron (Fe_2O_3)	0.35	0.12	0.13	1.70	0.88	—	0.25	1.30	0.45	1.10	Oxide of iron (Fe_2O_3)
Calcium oxide (CaO)	49.25	53.00	54.20	49.00	49.57	48.96	52.20	51.69	54.25	51.10	Calcium oxide (CaO)
Magnesium oxide (MgO)	0.67	0.16× (0.266)	0.10	0.40	0.22	0.98	0.20	0.03	0.77	0.10	Magnesium oxide (MgO)
Sodium oxide (Na_2O)	1.28	1.19× (1.60)	0.27	0.10	0.186	—	0.42	0.27	0.80	0.20	Sodium oxide (Na_2O)
Potassium oxide (K_2O)	0.10	0.16	0.06	—	0.09	—	0.01	0.05	0.02	0.07	Pôtassium oxide (K_2O)
Chlorine (Cl)	0.03	0.005	Traces	0.10	0.006	0.40	0.14	0.12	Traces	Traces	Chlorine (Cl)
Fluorine (F)	3.42	4.24	4.17	2.40	3.87	2.95	3.85	3.75	4.00	3.15	Fluorine (F)
Manganese Oxide (MnO)	—	0.0025	—	1.00	—	—	—	—	—	—	Manganese oxide (MnO)
Chromium	—	0.045	—	—	—	—	—	—	—	—	Chromium
Water of hydration, etc.	—	—	—	—	—	—	1.74	—	—	—	Water of hydration, etc.
Undertermined	—	—	—	—	—	0.53	—	—	—	—	Undetermined
To deduct:	101.25	—	101.57	—	101.44	100.00	101.63	—	—	101.17	To deduct
Oxygen corresponding to chlorine and fluorine	1.44	—	1.76	—	—	—	1.63	—	—	1.23	Oxygen corresponding to chlorine and fluorine
				—	—	—	—	—	—	—	
	99.81	—	99.81	—	—	—	—	—	—	99.94	
Undertermined-losses	0.19	—	0.19	—	1.63	—	—	—	—	0.06	Undetermined-losses
				—							
	100.00		100.00		99.81	—	100.00	—	—	100.00	
B.P.L. grade	65/68%	75%	80.82%	63/65%	77%	65/66%	70/72%	80/82%	75/77%	80/83%	B.P.L. grade

[Fertilizer Statistics, 1970-71, 375]

× One elemental basis. The equivalents are given in brackets.

Source — @ International Superphosphate and Compound Manufacturers' Association Ltd., London.

* The Minerals and Metals Trading Corporation of India Ltd., New Delhi

** Rallis India Ltd., Bombay.

TABLE 2—IMPORTS OF FERTILIZERS IN INDIA, TONNES

Country	1971			1970		
	April to June	July to Sept.	Total	April to June	July to Sept.	Total
1. **Ammonium Sulphate (20.6%N)**						
U.S.S.R.	—	—	—	14,558	13,910	28,468
2. **Urea (45%N)**						
U.S.A.	4,281	—	4,281	65,425	19,379	84,804
Urea (16%N)						
West Germany	—	—	—	2,142	—	2,142
Iran	4,091	—	4,091	—	—	—
Canada	—	—	—	12,960	20,565	33,525
Italy	—	—	—	—	31,603	31,603
Saudi Arabia	3,812	—	3,812	—	—	—
U.S.S.R.	15,950	8,158	24,108	9,234	1,984	11,218
Rumania	—	10,882	10,882	—	—	—
U.K.	—	1,076	1,076	—	—	—
Poland	37,435	10,798	48.233	20.000	—	20,000
Hungary	9,804	—	9,804	—	—	—
Bulgaria	33,080	48,360	81,440	—	—	—
Norway	12,300	12,501	24.801	—	—	—
Kuwait	—	100	100	3,400	16,000	19,400
Japan	—	—	—	13,022	1,707	14,729
France	45,051	6,553	51,604	—	—	—
Total	161,523	98,428	889,951	60,758	71,859	132,617
3. **Calcium Ammonium Nitrate (26%N)**						
West Germany	—	—	—	—	14,026	14,026
France	7,550	—	7,550	—	18,650	18,650
Norway	—	—	—	—	7,000	7,000
Holland	—	—	—	—	4,825	4,825
Italy	—	20,245	20,245	—	—	—
Rumania	—	49,623	49,623	—	—	—
Total	**7,550**	**69,868**	**77,418**	—	**44,501**	**44,501**
4. **Muriate of Potash (60%K_2O)**						
East Germany	10,318	9,155	19,473	—	10,187	10,187
Canada	93,563	152.590	246.153	—	—	—
West Germany	—	10,500	10,500	—	—	—
Total	**103,881**	**172,245**	**276,126**	—	**10,187**	**10,187**
5. **Sulphate of Potash (50%K_2O)**						
West Germany	—	—	—	3,861	3,139	7,000
6. **Nitrophosphate (20-20-0)**						
West Germany	—	—	—	14,881	2,541	17,422
France	—	15,099	15,099	—	—	—
Total	—	**15,099**	**15,099**	**14,881**	**2,541**	**17,422**
7. **Diammonium Phosphate (18-46-0)**						
U.S.A.	—	68,451	68,451	—	—	—
Canada	8.845	41,584	50,429	—	12,026	12,026
Total	**8,845**	**110,035**	**118,880**	—	**12,026**	**12,026**

[*Continued*]

TABLE 2—IMPORTS OF FERTILIZERS IN INDIA, TONNES—(*continued*)

Country	1971			1970		
	April to June	July to Sept.	Total	April to June	July to Sept.	Total
8. **NPK Complex Fertilizers**						
10-26-26 U.S.A.	15,346	20,733	36,079	—	4,818	4,818
12-32-16 U.S.A.	9.109	21,359	30,468	—	10,532	10,532
13-13-13 Greece	—	—	—	—	22,085	22,085
14-14-14 Canada	—	5,000	5,000	—	—	—
14-36-12 U.S.A.	10,500	10,000	20,500	—	10,000	10,000
14-28-14 Canada	—	10,000	10,000	—	—	—
15-15-15 U.S.A.	—	—	—	—	49,052	49,052
,, Canada	—	48,500	48,500	—	28,538	28,358
Total (15-15-15):	—	**48,500**	**48,500**	—	**77,410**	**77,410**
Grand Total N	83,879	101,680	185,559	63,365	76.511	139,876
Grand Total P_2O_5	14,754	80,236	94,990	2,976	28,745	31,721
Grand Total K_2O	69,036	122,729	191,765	1,930	26,302	28,232

[*FAI Inf. Serv.*, **13** (4) (1972), 12]

EDITOR'S NOTE

TECHNOLOGY accepts research papers from scientists and technologists outside FCI Ltd., provided these are:

(i) original and related to science and technology

(ii) approved by external referees chosen by the Editor, and

(iii) communicated from reputed institutions and written by workers with adequate experience.

Papers for publication in TECHNOLOGY are, therefore, welcome. These should be sent in duplicate (complete with illustrations and abstracts) to the Editor. Short communications, research notes, etc. are also accepted. Books, reports, proceedings of symposia, conferences, etc., meant for review in this journal, are welcome.

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TABLE 3—PRICES OF FERTILIZERS IN INDIA

The following are the current prices of fertilizers

(For materials packed in 100 kg bags)

Fertilizer		Price (Rs. per tonne)	
1. Ammonium sulphate (white)		529.00	
2. ,, (coloured)		429.00	
3. Ammonium sulphate nitrate		626.00	
4. Urea (46%N)		923.00	
5. Urea (45%N)		904.00	
6. Calcium ammonium nitrate—20.5% N		473.00	
7. ,, 25.0% N		545.00	
8. ,, 26% N		575.00	(imported)
9. Ammonium chloride—25% N (imported)		540.00*	
10. ,, (indigenous)		545.00	in U.P. and Bihar
		555.00	in M.P., Eastern Rajasthan & West Bengal, Haryana & Andhra Pradesh
		570.00	in Gujarat, Maharashtra, Punjab and Western Rajasthan
11. Ammonium phosphate sulphate (16-20-0)		915.00	in Kerala
		935.00	in Tamil Nadu, Mysore and Andhra Pradesh
12. Ammonium phosphate (20-20-0)		894.00	(imported)
13. Ammonium nitrophosphate (20-20-0)		880.00	(imported)
14. Diammonium phosphate	(18-46-0)	1,217.00	(imported)
15. ,,	(18-46-0)	1,345.00@	(indigenous)
16. Nitrophosphate (Suphala)	(20-20-0)	900.00	
17. Urea ammonium phosphate	(28-28-0)	1,252.00	
18. Urea ammonium phosphate	(20-20-0)	938.00	
19. ,,	(22-22-11)	1,126.00	
20. N.P.K. Compound Mixtures	(13-13-13)	782.00	(imported)
21. ,,	(14-14-14)	830.00	,,
22. ,,	(15-15-15)	912.00	,,
23. ,,	(14-28-14)	1,137.00	,,
24. ,,	(12-24-12)	915.00	
25. Superphosphate (16%W.S. P_2O_5)		291.18*	(ex-factory)
26. Triple superphosphate		875.00*	(,,)
27. Muriate of Potash	(61% K_2O)	523.00	F.O.R. despatching station; Freight prepaid to destination station)
28. ,,	(40% K_2O)	300.00	
29. ,,	(60% K_2O)	473.00	
30. ,,	(50% K_2O)	393.00	
31. Sulphate of potash	(48.1% K_2O)	731.00	

Notes: 1. The above prices include 10 per cent excise duty brought into force from 1-3-1969 except in the case of fertilizers marked with*.

2. To work out comparable maximum retail prices of superphosphate and triple superphosphate, an average figure of Rs. 50/- a tonne should be added to the respective prices shown above. Similarly, an amount of Rs. 30/- a tonne should be added to the prices of fertilizers under items No. 22 to 26 to arrive at their comparable maximum retail prices.

3. From October 1, 1971, retail price of urea sold by Shriram Chemical Industries is Rs. 913 per tonne.

[*Fert. Marketing News*, **2** (11) (1971), 18]

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TECHNOLOGY Vol. 9 (1972), No. 1, Jan-March

Some of the papers, short communications, research notes, etc. accepted for publication in the above issue of TECHNOLOGY are as follows:

Papers

MECHANICAL ACTIVATION OF CO-CONVERSION CATALYST: CHANGES IN SURFACE AREA, PORE STRUCTURE AND ACTIVITY
by B. R. Arora, H. Mahapata, B. Achari, N. C. Ganguli and S. P. Sen

APPLICATION OF DIFFERENTIAL THERMAL AND THERMOGRAVIMETRIC TECHNIQUES TO THE STUDY OF FERRIC OXIDE AND FERRIC OXIDE-CHROMIUM OXIDE TYPE CONVERSION CATALYSTS
by B. R. Arora, N. K. Mandal, R. L. Chowdhury N. C. Ganguli and S. P. Sen

A STUDY OF THE CHANGES IN SURFACE AREA AND SURFACE EXCESS OXYGEN AS A FUNCTION OF CALCINATION TEMPERATURE IN NICKEL OXIDE AND NICKEL OXIDE-ALUMINA
by B. R. Arora, N. K. Mandal, R. K. Banerjee, N. C. Ganguli and S. P. Sen

NAPHTHA REFORMATION CATALYST: EVALUATION OF ITS STRUCTURAL STABILITY
by D. K. Mukherjee, S. K. Ghosh, M. Sundaram and S. P. Sen

HYDRO-DESULPHURIZATION OF LOW BOILING LIQUID HYDROCARBON FRACTION BY ALKALIZED IRON
by P. K. Gaur, N. B. Bhattacharyya and S. P. Sen

DEVELOPMENT OF REPRODUCIBLE AND LASTING GAS-SOLID-LIQUID COLUMN FOR THE ANALYSIS OF LIGHT HYDROCARBONS
by D. S. Mathur and N. C. Saha

SOLUBILITIES OF CALCIUM SULPHATE DIHYDRATE IN NITRIC AND PHOSPHORIC ACID SOLUTIONS
by A. D. Pandey, K. K. Mallick and A. K. Roy

AUTOMATIC MAGNETIC FIELD MARKER
by G. Datta and P. K. Ghosh

POLAROGRAPHIC EVALUATION OF THERMODYNAMIC FUNCTION: SYSTEM COPPER (II)-BIURET
by M. B. Mishra, S. S. Chatterjee and R. M. Sanyal

THERMAL CONDUCTIVITY, VISCOSITY AND DIFFUSIVITY OF A GAS MIXTURE
by S. R. Ghosal, S. P. Sinha, B. Banerjee, K. Karkun and A. D. Majumdar

EFFECT OF TEMPERATURE REGIMES AND TIME INTERVALS ON THE AVAILABILITY OF PHOSPHATES FROM DIFFERENT SOURCES
by J. D. Naphade and S. P. Dhua

FLOW PROPERTIES OF BULK SOLIDS
by N. K. Roy and H. H. Jethanandani

TENSILE PROPERTIES OF BOILER QUALITY CARBON STEEL PLATES AT ELEVATED TEMPERATURES
by N. K. Roy and S. R. Ramachandran

INERTIA EFFECTS IN RHEODYNAMIC LUBRICATION OF A SLIDER BEARING
by R. L. Batra

Short Communications

SELECTION OF OPERATING PARAMETERS FOR HYDROGEN SULPHIDE ABSORPTION BY IRON OXIDE
by A. B. Ghatak, N. C. Mehta and N. B. Bhattacharyya

AUTORADIOGRAPHY IN RADIOTRACER ADSORPTION STUDIES ON METAL SURFACES
by T. Sahu, I. S. Mishra and S. K. Das